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SAFETY STUDIES OF LITHIUM-SULFUR DIOXIDE CELLS.(U)

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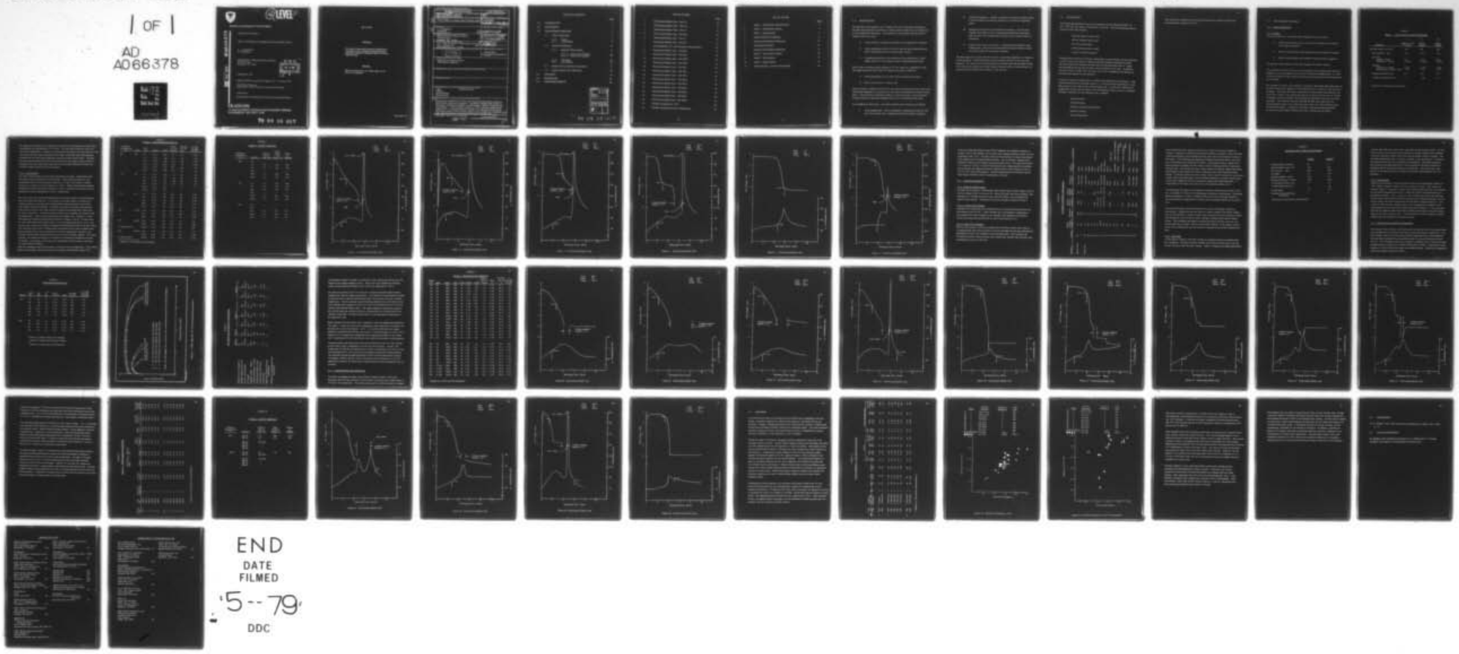

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SAFETY STUDIES OF LITHIUM-SULFUR DIOXIDE CELLS

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HONEYWELL POWER SOURCES CENTER
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Hermetically sealed SO_2 "D" cells were fabricated and tested to improve safety during use/abuse conditions. Variables evaluated were wrap configurations, cathode processing, cathode density, lithium content and SO_2 concentration. At 2A constant current, at -20°F and room temperature, respectively, no venting occurred to 200% of the theoretical SO_2 content. Discharge efficiency had the most influence on the safety and cathode development contributed most to improving the overall cell efficiency.

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1.0 INTRODUCTION

The objective of this program was to explore the cause-and-effect relationship between cell performance and safety in lithium-sulfur dioxide cells as determined by cell composition and design. The quantitative relationships obtained will be useful in three main ways:

1) In the avoidance of inherently unstable cell compositions or designs.

2) In the availability of data on which to make the best tradeoff between safety and performance for any particular mission.

3) In allowing prediction of the sensitivity of the safety factor to poor quality control, to cell leakage and poor handling during storage.

State-of-the art spirally would cylindrical "D" size cells were upgraded for high rate applications and tested under the following use/abuse conditions:

1) Forced discharge at 2A to 200% of the theoretical SO_2 content

2) Short circuit across a resistor load

These use/abuse conditions are the most commonly encountered in battery operation. Cell design safeguards are necessary as they cannot be eliminated by battery design alone. A third common use/abuse condition, electrical charge, can be prevented by diode protection and proper handling and was not considered for this study.

To accomplish the objectives, a four phase program was carried out as follows:

I. Wrap Configuration - Three independent configurations with over 600 cm^2 active surface were compared under the use/abuse conditions.

II. Cathode Development - Cathode composition and process improvements to increase high rate discharge efficiency as a means of improving safety.

III. Cathode Process and SO_2 Concentration Variations - The two best cathodes from Phase II were compared for performance and safety under the best wrap configuration of Phase I over a range of SO_2 concentrations.

IV. Cathode Density and Li/SO_2 Ratio - Continuing the same basic wrap configuration, cells of varied cathode density and low lithium content were tested under the use/abuse conditions.

The design goal was to limit internal reactions, preventing explosions or venting on forced discharge. Maintaining safe venting (no flame) on short circuit was also expected. No reaction on forced discharge was achieved with one particular design at the end of the program and trends towards improved safety by basic design considerations also emerged from analysis of test results.

2.0 BACKGROUND

The cell design proposed for use on this program was the Honeywell G3091 "D" cell. This cell was rated at 10 amp hours at 350 mA. Some of the physical characteristics of this cell included:

- Hermetic glass-to-metal seal
- 260 cm^2 cathode surface area
- 72% wt SO_2 electrolyte
- 0.020 inch thick lithium anode
- 2 layers of Webril separator

Testing of this cell prior to contract award under a 2 amp constant current discharge at -20°F (worst case abusive condition proposed) divulged unexceptable results. The cells would vent with flame shortly after the total discharge time at 2 amps had exceeded the theoretical amp hours of SO_2 available in the cells. In addition, run times above 2.0 volts were very poor and it was concluded that the design was basically unacceptable for this program.

To meet the program requirements, a higher rate cell design was necessary. High efficiency designs were generally rated at 1 - 2 mA/cm^2 which would require a four fold increase in the surface area of the standard cell. A 4 mA/cm^2 maximum was proposed for the 2A rate requiring a 500 cm^2 minimum surface area for a redesign. Variables considered for the redesign were as follows:

- Anode thickness
- Cathode loading
- Separator material and thickness
- Materials balance
- Wrap configuration

The redesign is reflected in the cell design parameters of Phase I and all subsequent designs in Phases II thru IV.

3.0 DEVELOPMENT PROGRAM

3.1 Wrap Configuration

3.1.1 Design

The three designs for evaluating wrap configuration were as follows:

1) Single cathode/single anode reverse wrap (cathode on the outside) with Celgard separator.

2) Double cathode/double anode standard wrap with Celgard separator.

3) Single cathode/single anode standard wrap with Webril separator.

The physical characteristics of the three designs are shown in Table I.

The reduction of lithium thickness to provide space for the longer electrodes was limited by cost and handling as well as electrochemical considerations. A 0.0075 ± 0.001 inch thick foil was chosen the most practical and became the starting basis for the design.

The cathode at the start of the program consisted of Shawinigan Black and teflon in an 80/20 weight ratio, applied to the aluminum grid by a wet slurry cast filtration technique. Thickness was easily controlled but carbon density was generally low. There was a choice of two separators; Webril, as used in the low rate "D" design, or Celgard, which was thinner and would provide additional volume for the active materials. The wrap was varied by allowing the final outer layer to be the anode (standard wrap) or the cathode (reverse wrap) or by using multiple layers of shorter electrodes. Variation of materials, quantities and design altered the electrochemical balance between the anode, cathode and electrolyte.

TABLE 1

BUILD 1 - WRAP DESIGN CHARACTERISTICS

	I	II	III
Separator	Single Reverse Celgard	Double Celgard	Single Webril
Cathode Surface Area cm^2	630	600	600
SO_2 Capacity - Ahr	10.0	10.8	10.0
Lithium			
Length - inches	27	14.5	27.3
Thickness - inches	0.0075	0.0075	0.0075
Cathode			
Thickness - inches	0.022	0.027	0.024
Carbon/teflon weight - gms	6.75	6.75	6.25
*C/SO_2 Coulombic Ratio	0.9	0.9	0.9
Li/SO_2 Coulombic Ratio	1.2	1.28	1.3

* Based on 1.44 Ahr/g mix theoretical.

All wraps used a double layer of separator between the electrodes and the electrolyte concentration was maintained at 72 wt % SO_2. The only other difference was in the anode lead configuration. Designs II and III used the standard 0.200 inch wide by 0.005 inch nickel lead perforated and staked to one edge of the anode width while design I continued this lead attachment diagonally through the entire anode length. Although this lead extention would have also been preferred for the equally long electrodes of design III, there was insufficient space due to the thickness difference between the 0.008 inch Webril and the 0.001 inch Celgard.

3.1.2 Test Results

Ten cells of each design were fabricated and tested for safety. Performance data was gained from the initial part of this testing. Cells were discharged at room temperature and in an environmental chamber at -20 and 130°F under a constant current of 2.0 amps to a cutoff voltage of 2.0 volts. Table 2 shows that all designs exceeded four hour performance standard at 130°F, but failed the four and two hour standards at room temperature and -20°F, respectively.

The same cells were further discharged until they either vented or a total discharge time of ten hours was reached. For reasons of personnel safety, the cells were contained within a bomb box in the environmental chamber placed in an enclosed room vented outside the building. In addition, the cells were held in an aluminum clamp which acted as a heat sink and were wrapped with heating tape to deactivate the cells if necessary. A thermocouple was placed on the outside case surface under the heating tape. Table 3 shows the results of the safety tests. Figures 1-6 show representative voltage and temperature profiles of designs I and III. In most cases, the cells vented before the ten hour limit. At room temperature and at -20°F, venting was more violent with a higher temperature differential and with flame (vent areas were charred); while at 130°F venting was more passive with a barely audible "pop". Cells unvented after 10 hours showed only a 20-40°F temperature rise due to the aluminum clamp which conducted heat away from the cell rather rapidly. For safety reasons, the current was raised to 8 amperes to deliberately neutralize the cells by venting. In all cases, case rupture was contained to the vent area, even when the cells vented with flame.

Cells from designs II and III were short circuited at room temperature. Both vented safely without flame within 4 minutes with surface temperatures below 150°F.

TABLE 2

BUILD 1 - PERFORMANCE RESULTS

Chamber Temperature, °F	Load	Cell No.	Li/SO_2	C/SO_2*	Time to 2.0V (Hours)	SO_2 Eff. to 2.0V (%)	C & Tef Ahr/gm to 2.0V
RT	2A	I-3	1.19	.81	3.3	61	1.08
		I-5	1.21	.84	3.3	62	1.05
		II-3	1.42	.86	3.1	58	.98
		II-4	1.50	1.01	3.8	73	1.04
		III-1	1.35	.78	2.0	40	.75
		III-4	1.40	.80	2.1	42	.76
-20	2A	I-6	1.23	.81	.6	11	.20
		I-9	1.25	.86	.65	12	.20
		II-5	1.45	.93	.80	15	.23
		II-6	1.42	.97	.95	18	.27
		III-5	1.32	.78	-	-	-
		III-11	1.43	.81	-	-	-
130	2A	I-1	1.23	.82	4.9	92	1.61
		I-8	1.27	.78	4.6	87	1.58
		II-2	1.38	.96	4.6	87	1.30
		III-2	1.36	.86	4.0	81	1.35
		III-6	1.33	.77	4.1	83	1.53
RT	2.67Ω	I-10	1.29	.83	9.1	86	1.47
		II-7	1.39	.94	9.5	88	1.35
		III-9	1.39	.83	7.5	74	1.28
RT	1.25Ω	I-12	1.36	.89	3.1	59	.95
		II-12	1.45	.95	3.8	72	1.08
(3 days at 130°)		III-12	1.43	.85	2.5	49	.82
RT	1.25Ω	I-11	1.38	.84	3.6	69	1.17
		II-10	1.49	.96	3.7	72	1.08
(5 days at 160°)		III-10	1.47	.81	3.0	59	1.04

* Based on 1.44 Ahr/g mix theoretical.

TABLE 3

BUILD 1 - SAFETY RESULTS

Chamber Temperature, °F	Cell No.	Time to Vent at 2.0A, Hrs	Case Surface Vent Temp., °F	Flame on Venting
RT	I-3	-	-	-
	I-5	5.5	266	Yes
	II-3	7.1	426	Yes
	II-4	-	-	-
	III-1	7.5	518	Yes
	III-4	6.4	555	Yes
-20	I-6	5.4	117	Yes
	I-9	5.3	147	Yes
	II-5	8.0	190	Yes
	II-6	-	-	-
	III-5	5.6	211	Yes
	III-11	6.4	154	Yes
130	I-1	-	-	-
	I-8	-	-	-
	II-2	6.8	187	No
	III-2	5.6	240	No
	III-6	5.5	214	No

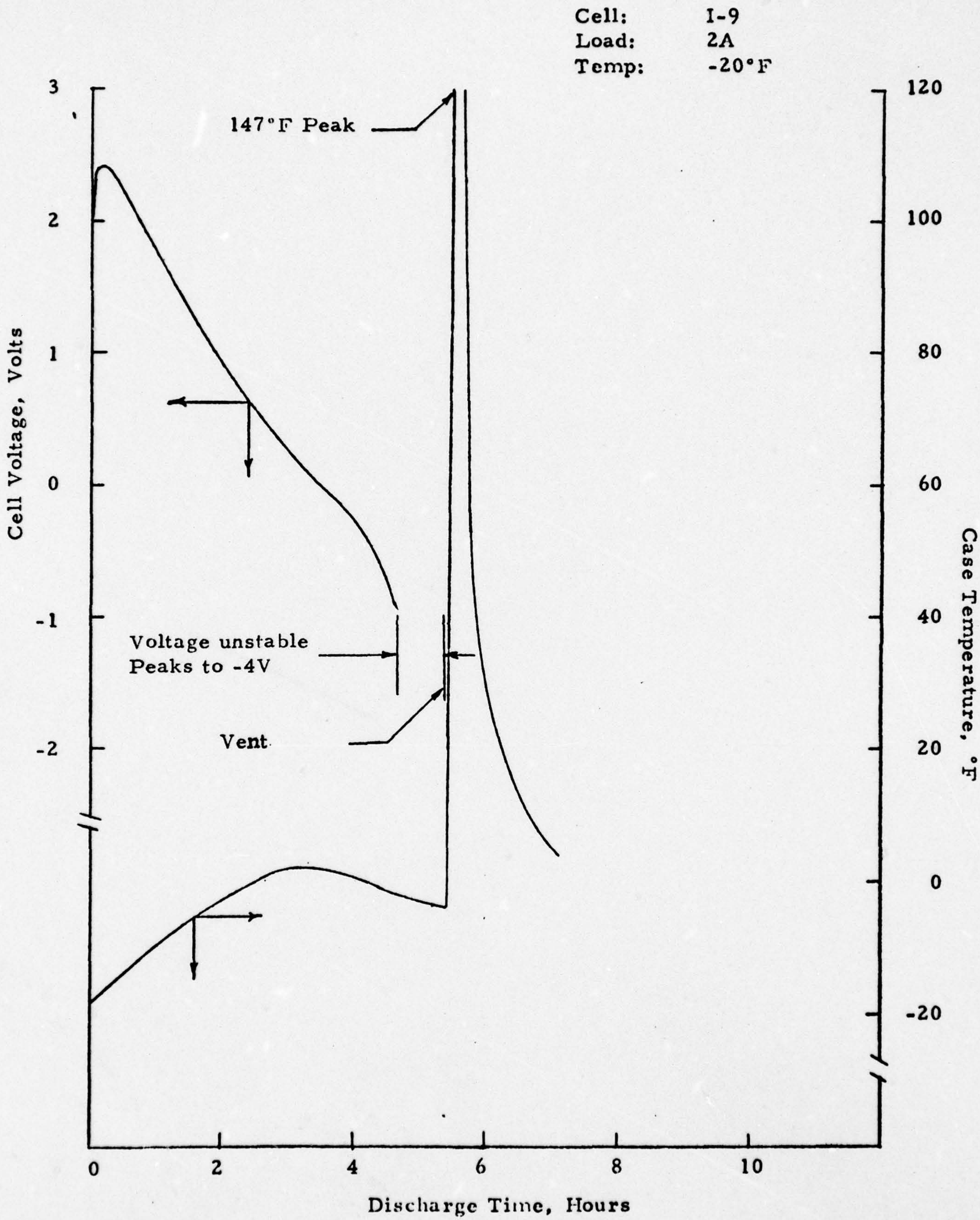

Figure 1. Performance/Safety Test

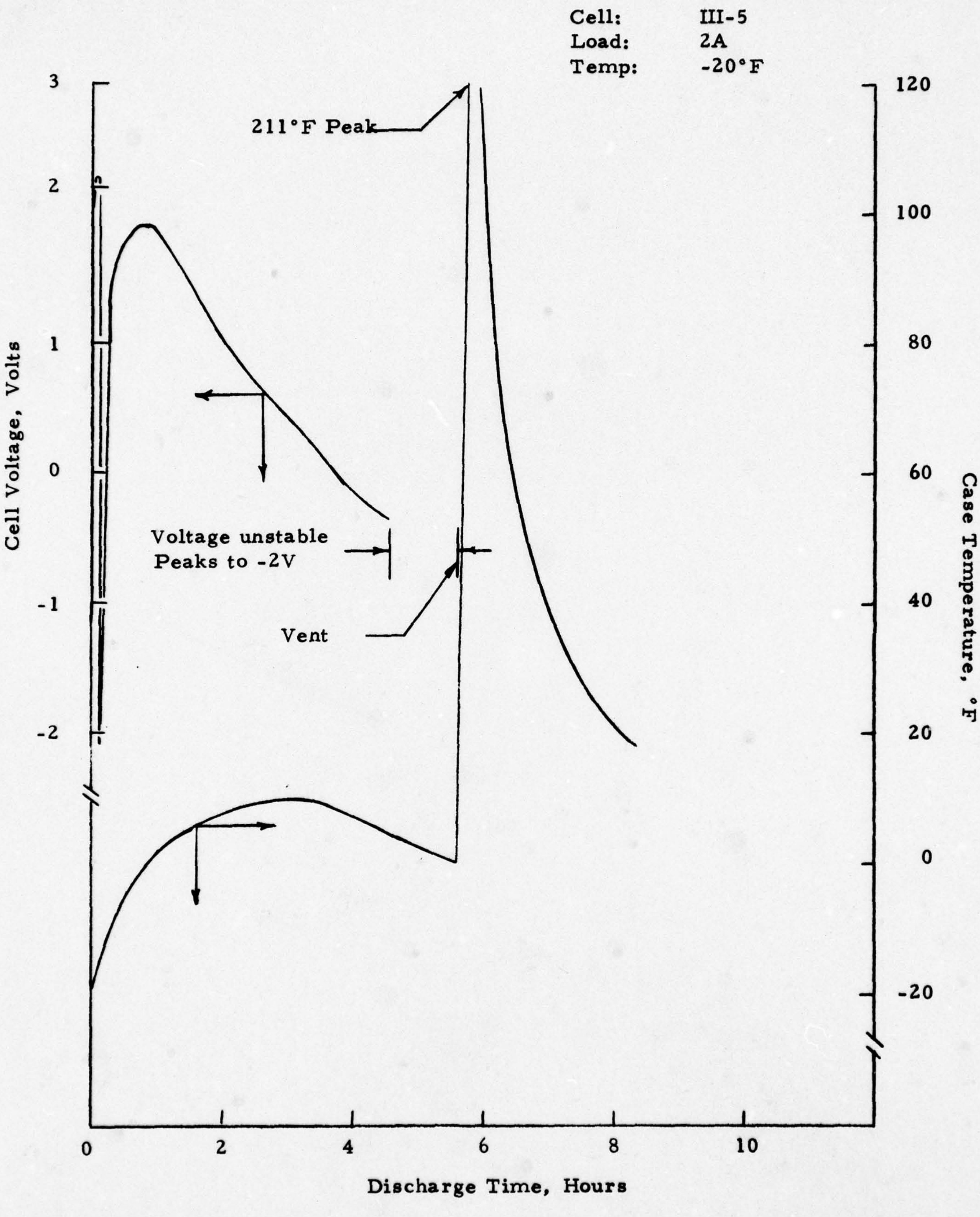

Figure 2. Performance/Safety Test

Cell: I-5
Load: 2A
Temp: Room

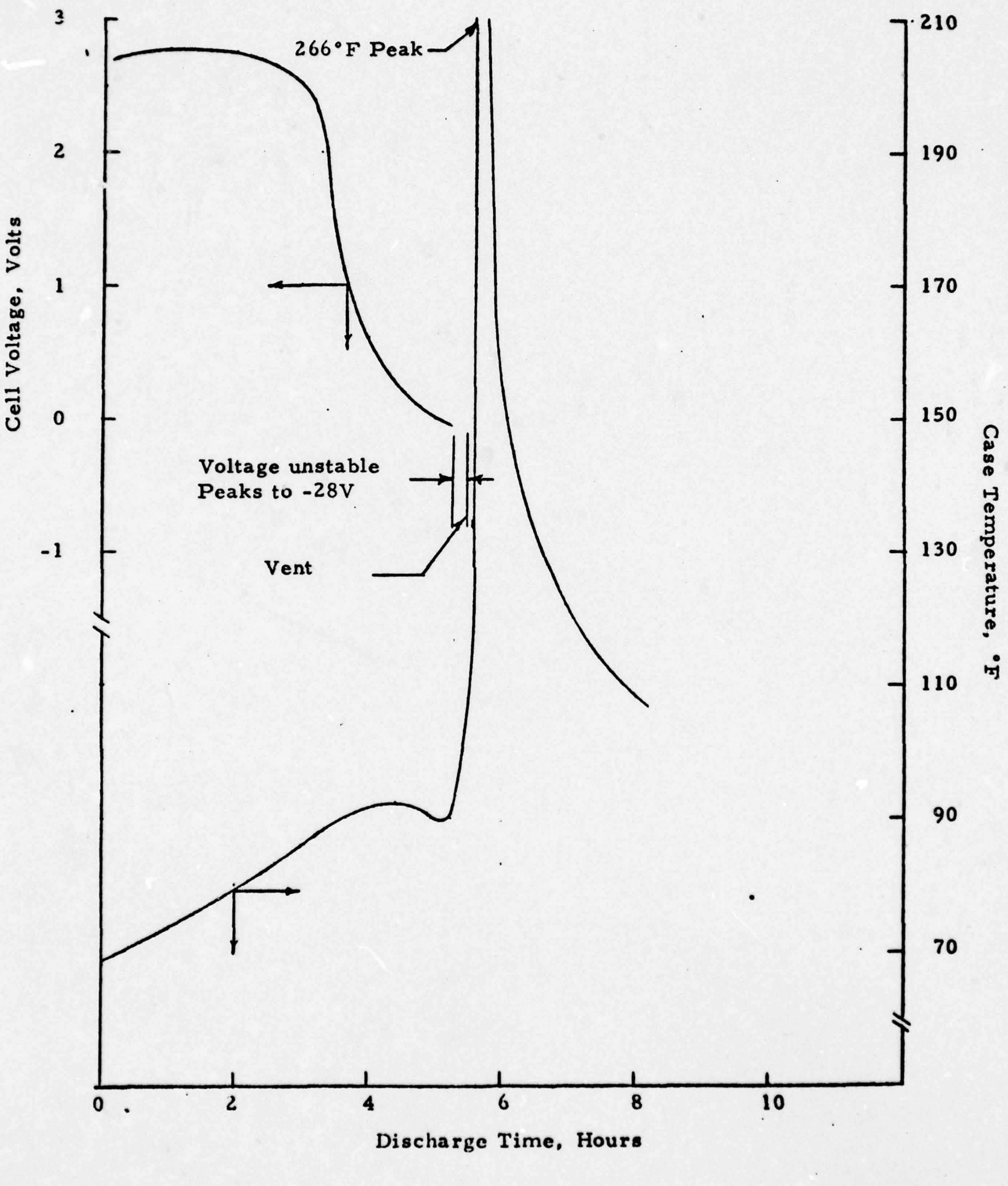

Figure 3. Performance/Safety Test

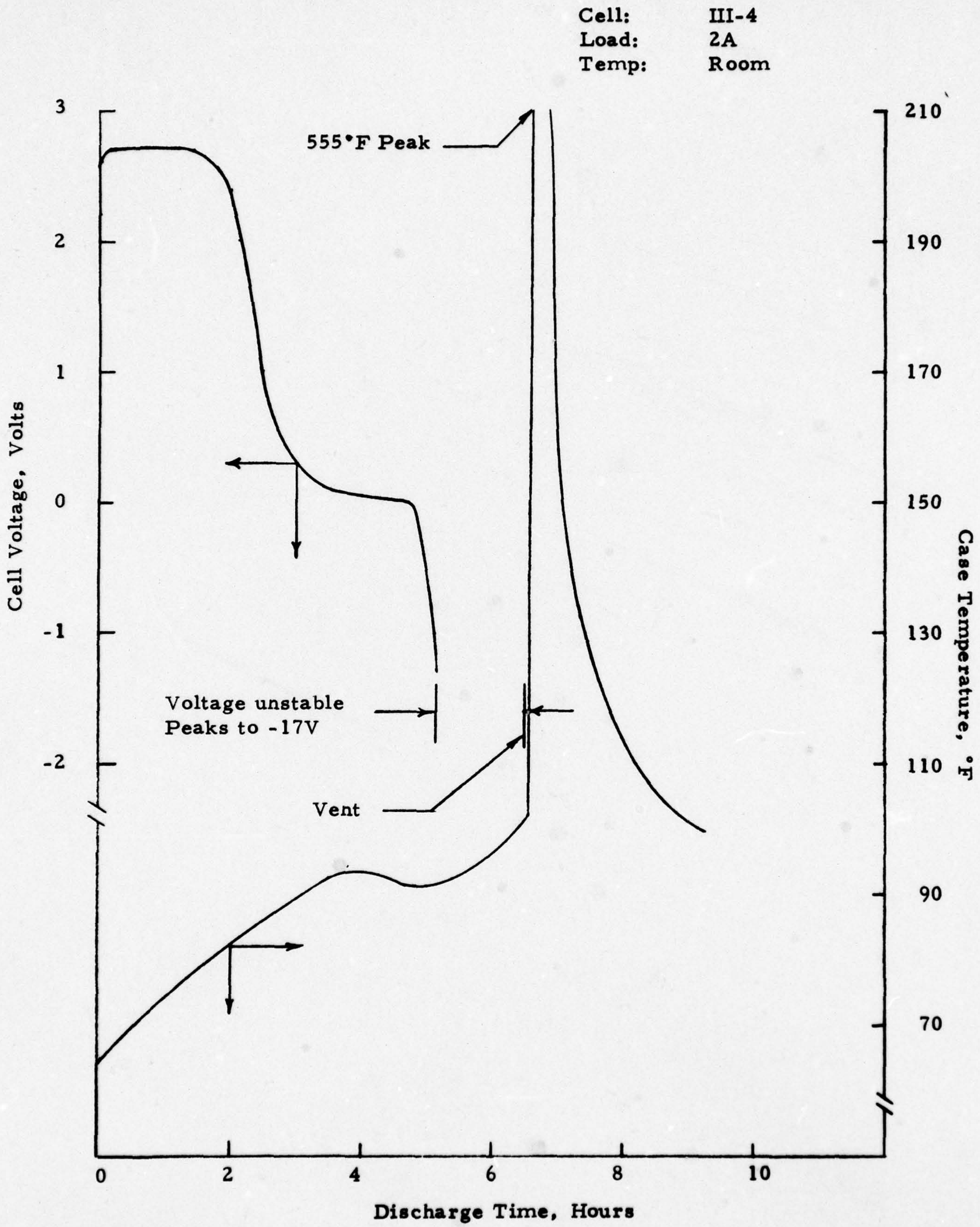

Figure 4. Performance/Safety Test

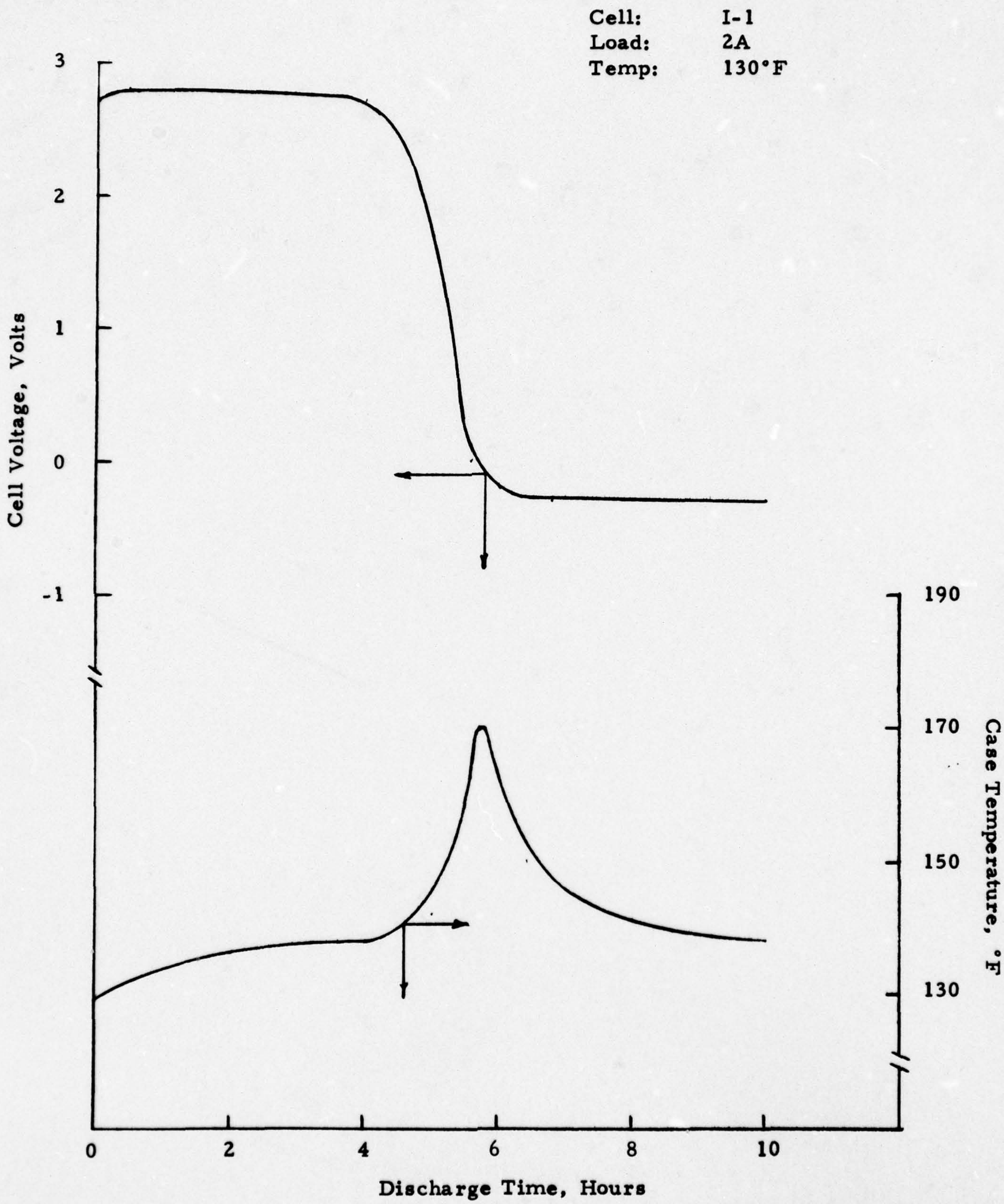

Figure 5. Performance/Safety Test

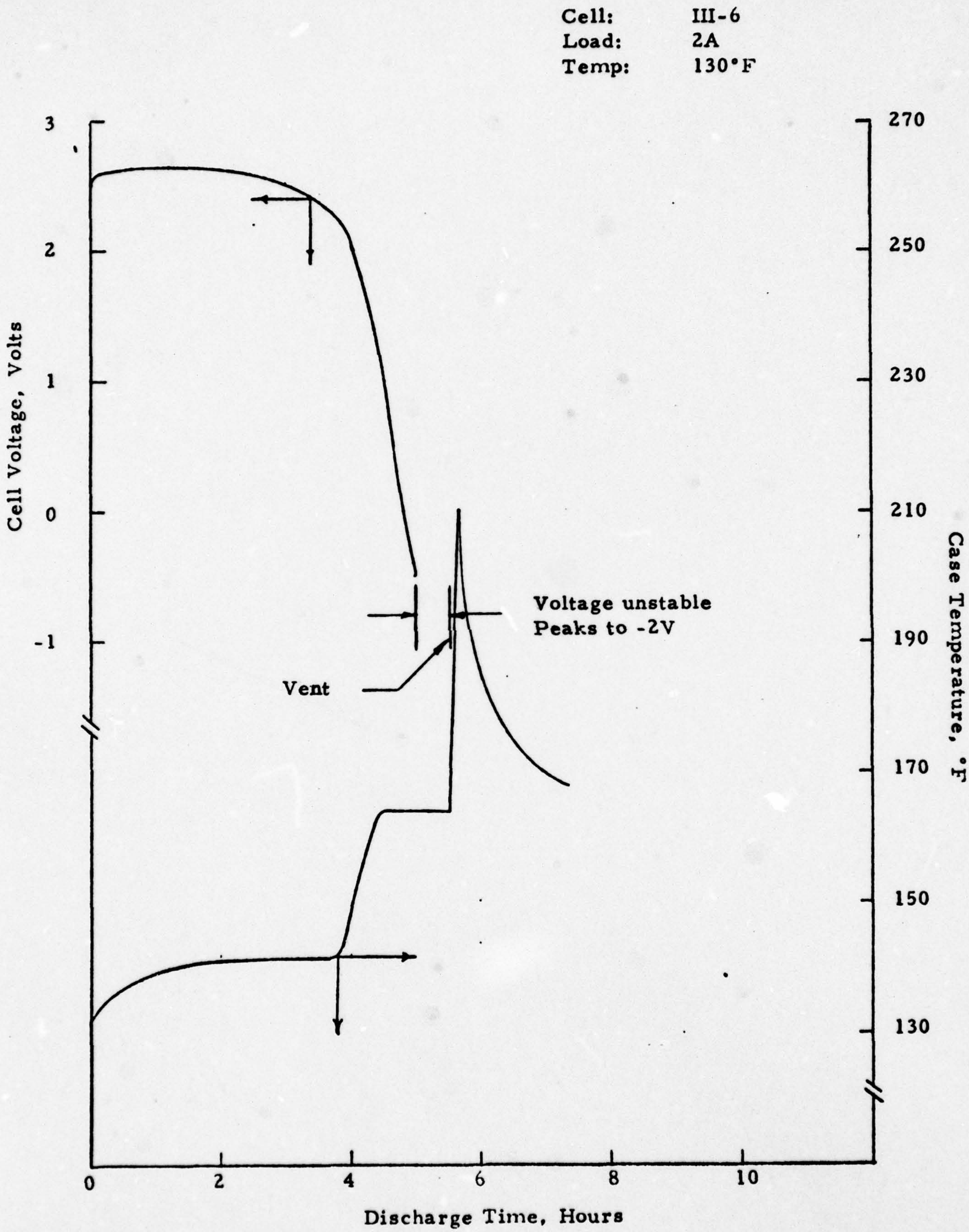

Figure 6. Performance/Safety Test

It was concluded that design III with Webril separator was definitely inferior to designs I and II with Celgard, and all three were lacking sufficient activity at room temperature and -20°F. The poor safety and low efficiency of these tests pointed to the cathode as the limiting design variable. The low cathode loading and the high teflon content of the cathode were the probable cause. The good performance (~9.0 Ah) at 2.67 ohm, or one-half the desired load, reinforced this conclusion. Also noted was the slight performance improvement by heat soaking the cells at 130° or 165°F before discharging. Cathode improvement was necessary before other design variables could be meaningfully evaluated.

3.2 Cathode Development

3.2.1 Reduced Teflon Content

The goal was to develop a mechanically sound cathode with a teflon content reduced from the standard 20% to as low as 5%. Slurry cast and roll form techniques, both equivalent for strength and performance with 20% teflon, were evaluated with reduced teflon content. Comparison of the new cathodes is shown in Table 4.

3.2.1.1 Slurry Cast Cathodes

Cathodes were fabricated by the standard slurry cast process with the teflon content reduced from 20 to5%. These cathodes were mechanically comparable to the standard 20% teflon cathodes as for strength, grid adherence and density. Their electrochemical performance in cells is discussed in 3.2.3.

3.2.1.2 Roll Form Cathodes

Prior to this contract, roll form cathodes with 20% teflon content were made on an experimental basis and had shown to be both mechanically and electrochemically equivalent to slurry cast cathodes at low discharge rates. The technique was to blend the carbon, teflon and water into a paste and, together with the grid, pass it between the rolls of a roll mill.

TABLE 4

CATHODE PROCESS COMPARISON

Process	Teflon%	Water Content Weight %	Thickness Inches	Shrink/ Swell on Drying %	Cathode Density gm/cc	Adherence to Grid	Surface Cracking	Comments
Slurry Cast	20	99	.022	N/A	.33	Very Good	None	
	5	99	.033	N/A	.33	Very Gocd	None	
Roll Form	20	63		-	-	Very Good	None	
	10	68		-	-	Good	Slight	
		66		-	-	Poor	Heavy	
		63		N/A	N/A	N/A	N/A	Grid Tore
	5	74		-16 to -12	.34	Poor	Heavy	
		70-71		-6.7 to +3	.30-.34	Fair-Good	Moderate	
		68		+3.0 to +6.7	.28-.30	Poor-Good	Mod.-Heavy	
		66		-	-	Poor	Heavy	
		63		N/A	N/A	N/A	N/A	Grid Tore
		70		-	-	Fair	Moderate	Triton X-100 Addition
		50		-	-	Poor	Heavy	80/20 : Propanol/ Water
		38		-3.0	.34	Good	Moderate	50/50 : Propanol/ Water
		68		+12.1	.28	Very Good	None	Rewet Dried Slurry
		0		N/A	.25	Very Good	None	Dried Slurry
		0	.025	N/A	.34	Very Good	None	Dried Slurry

It was found that water content becomes more critical as the teflon content is lowered. Cathodes of reasonable mechanical strength consisting of 5 and 10% teflon could be fabricated by this technique but they were rarely of the quality of those of 20% teflon. With little apparent differences between the reduced levels, the effort was concentrated on the preferred 5% teflon. Increasing the water content of the paste promoted shrinkage and led to heavy surface cracking and loss of adherence during drying. Decreasing the water content reduced the density without improving grid integrity during drying and further reductions led to grid distortion during rolling. It became evident that water content control was too critical for the process, as day to day irreproducibility occurred despite attempts to carefully measure and control water additions and losses during the mixing and rolling operations. A compromise at 70% water was used for the cell build described in 3.2.2.

A brief attempt was made to use additives to improve adherence and reduce cracking. An addition of Triton X-100 wetting agent showed no improvement. Increasing propanol additions to a 50/50: Propanol/Water level were somewhat beneficial but environmental considerations for large scale processing reduced its attractiveness.

A dried carbon/teflon mix was formed from a slurry by filtering, drying and micronizing. Initially the mix was rewet to a water content of 68% before rolling, with very good results. Similar results were achieved by directly feeding the dried mix through the roll mill with the grid, forming a cathode which did not require drying. This technique represents a significant advance towards a low cost continuous production cathode. Still to be perfected, however, is the density control which varies considerably with the volume of material in the nip and cathode thickness.

3.2.2 Cell Build

A cell build to evaluate a 5% teflon cathode was initiated before the cathode study was completed. The best 5% teflon cathodes at the time were the slurry cast and the wet roll form with 70% water content. Table 5 compares the design parameters

TABLE 5

REVERSE WRAP DESIGN COMPARISON

	Build 1	Build 2
Cathode Teflon Content %	20	5
Cathode Surface Area cm^2	630	493
SO_2 Capacity - Ahr	10.8	10.8
Li Length	27	22.5
Cathode Length - inches	29.5	24
Cathode Thickness - inches	.022	.034
*C/SO_2 Ratio Slurry Cast	.9	.94
*C/SO_2 Ratio Roll Form	-	.96
Li/SO_2 Ratio	1.2	.99
Separator Layers Between Electrodes	2	2

*Based on 1.44 Ahrs/gm mix theoretical

of these cells with those of the same construction of the previous build. The 22% surface area loss and reverse wrap (cathode on outside) retention were designed to permit maximum cathode volume and reduced lithium content for safety. The resulting cathodes had over 7.5 grams of carbon, or an equivalent of 1.0 Ah/g for the required 8 Ahrs at room temperature 2A discharge. The double separator layer between electrodes and the 10.8 Ah theoretical of 72% SO_2 electrolyte remained as before to provide continuity for evaluation. These cells were heat soaked for 48 hours to weed out leaders and provide conditioning for the -20°F discharge.

3.2.3 Test Results

Cells were discharged at room temperature and in an environmental chamber at -20°F under a constant current of 2A to a cutoff of 2.0 volts. The results are shown in Table 6. In general, the roll form outperformed the slurry cast cathodes at both room temperature and -20°F. Roll form cell R6 was discounted due to difficulties in filling. The 1.3 hours at -20°F achieved by the two roll form and the one slurry cast cathode cells with 5% teflon was a 100% improvement over the earlier build of the same construction with 20% teflon cathodes (Figure 7). The 4 hours by both roll form cathode cells at room temperature represents a 21% improvement and also meets the ECOM performance standard. It was concluded that both the reduced teflon levels and the added carbon weight more than compensated for the loss of surface area. A teflon content of 5% with maximum cathode loading was to be retained for the next iteration.

3.3 Cathode Process and SO_2 Concentration

Five percent teflon cathodes, fabricated from both wet and dry roll form processes, were compared for performance and safety in the high rate cell construction. The basic design, with the reverse wrap and double separator layer, was maintained with electrodes extended from the previous build to increase the surface area to 605 cm^2. The resulting Li/SO_2 ratio increased to slightly over 1.0 and the adjusted cathode thickness resulted in a similar C/SO_2 ratio as build 2. Electrolyte concentrations of 72 and 68% SO_2 were used as an added variable. Parametric comparison to the other builds is shown in Table 7.

TABLE 6

PERFORMANCE RESULTS

Temp.	Cell* No.	Li/ SO_2	C** SO_2	Time to 2.0V	Peak	SO_2 Eff to 2.0V	C & Tef Ahr/gm to 2.0V
-20	S1	.97	.93	1.35	2.33	.25	.39
	S4	.98	.94	1.05	2.36	.20	.30
	S5	.98	.94	1.05	2.28	.20	.30
	R1	1.01	.98	1.30	2.37	.25	.37
	R4	.99	.94	1.32	2.30	.25	.39
	R6	.98	.90	.62	2.20	.12	.24
RT	S2	.98	.94	3.53	2.73	.67	1.02
	S3	1.01	.96	3.37	2.70	.65	.98
	R3	.99	.99	4.03	2.75	.78	1.12
	R5	.99	.97	4.02	2.65	.77	1.13

*Prefix "S" denotes Slurry Cast Cathode
Prefix "R" denotes Roll Formed Cathode

**Based on 1.44 Ahr/gm mix theoretical

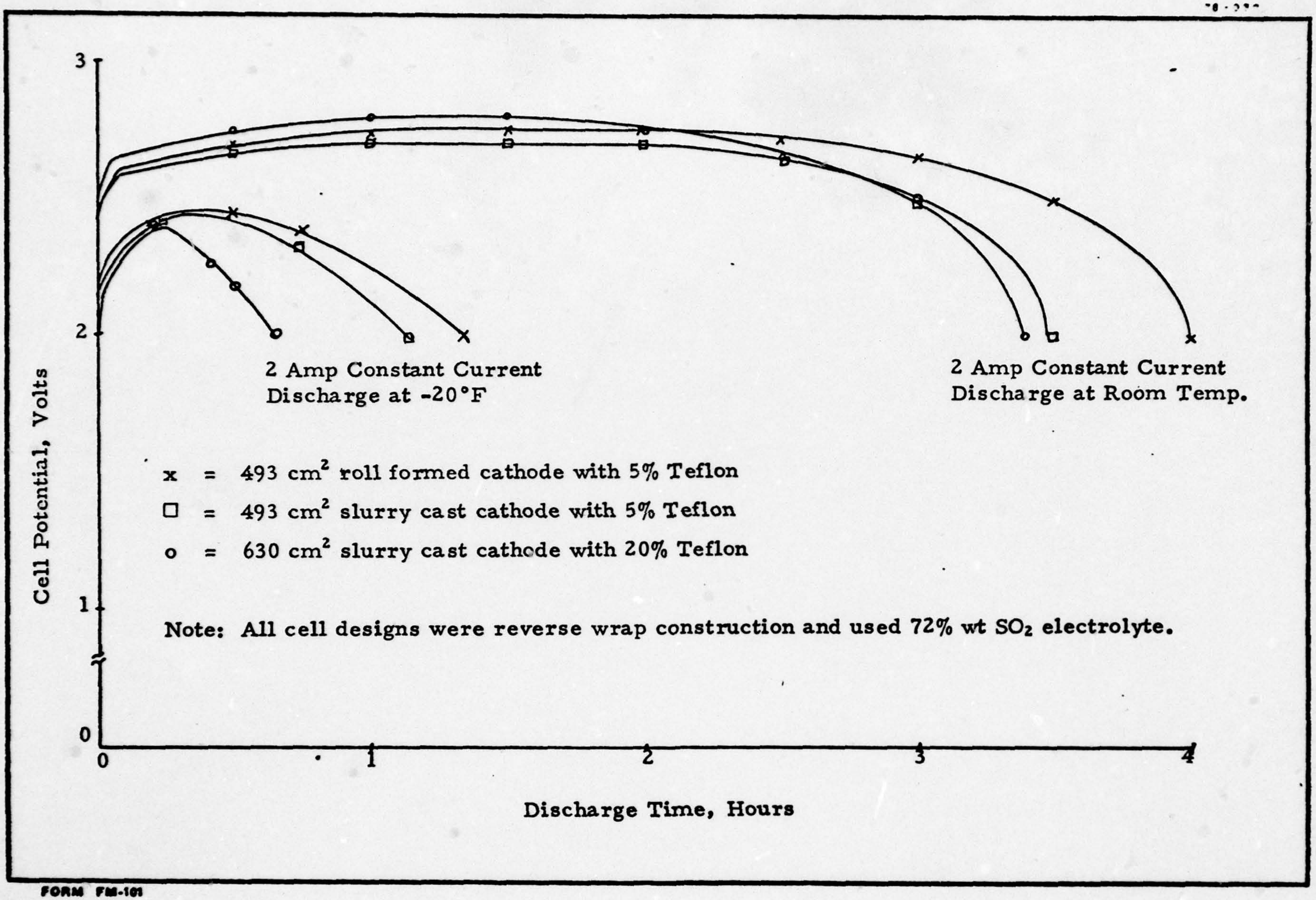

Figure 7. G3091 High Rate "D" Cell Discharge Characteristics

TABLE 7

REVERSE WRAP DESIGN COMPARISON

	Build 1	Build 2	Build 3			Build 4	
Cathode Teflon Content %	20	5	5	5	5	5	5
Cathode Surface Area cm^2	630	493	605	605	605	540	580
SO_2 %/ - Ahr Capacity	72/10.8	72/10.8	72/10.8	68/10.2	72/10.6	68/10.7	68/10.7
Li Length	27	22.5	26.5	26.5	26.5	22.5	24.5
Cathode Length - Inches	29.5	24	29	29	29	26	28
Cathode Thickness - Inches	.022	.034	.025	.025	.025	.035	.031
*C/SO_2 Ratio Slurry Cast	.9	.94	---	---	---	---	---
*C/SO_2 Ratio Roll Form	---	.96	.95	1.0	.85	.90	1.15
Li/SO_2 Ratio	1.2	.99	1.01	1.08	1.04	.87	1.00
Separator Layers Between Electrodes	2	2	2	2	1	2	1

*Based on 1.44 Ahrs/gm Mix Theoretical

Also shown for build 3 in Table 7 is a group of cells constructed with the wet roll cathodes and a single separator layer. These cells were intended as alternate means of improving the efficiency level of the cell, especially at -20°F.

All cells were stored at 165°F for 48 hours to separate possible leakers and to condition the cells for better performance. The results of the performance testing is shown in Table 8 with WR and DR referring to wet and dry roll form cathodes, respectively. The 2A constant current discharge indicated the cells with dry roll form cathodes were superior at both -20°F and room temperature over the 68 and 72% SO_2 concentration range tested. The single separator cells did not perform well but this data was coulded by the SO_2 concentration (the 72% SO_2 used is less conductive than 68%), the lowest C/SO_2 ratios of the build and the looseness of the wrap in the case.

Safety testing of the wet and dry roll comparison cells was significantly improved over build 1. None of the six room temperature cells vented after 10 hours at 2A and only one of six cells vented at -20°F. The cell that did vent was a single separator wrap WR17 and 72% SO_2 with a poor 1.0 hour discharge to 2.0V at -20°F. Figures 8 to 16 compare the voltage and case temperature profiles of the vented cell to representative cells that did not vent during the discharge testing sequence.

The performance and safety data of this build indicated the dry roll form cathode process was at least comparable to the wet roll form process. Overall, this design with the 68% SO_2 concentration was closest to achieving the 2.0 and 4.0 hour 2A discharge goals at -20°F and room temperature respectively while providing safe operation during extended discharge to 200% of the SO_2 theoretical capacity. The design, cathode, lithium content, electrolyte and the efficiency to 2.0V all appeared to influence the safety but the relative effects were not definitive from the test data.

3.4 Cathode Density and Li/SO_2 Ratio

To further investigate the effect of the lithium content on safety, cells were fabricated with 5% teflon cathodes of 540 and 580 cm^2 surface area Li/SO_2 ratios of 0.87 and 1.00 respectively. The former group used the double separator configura-

TABLE 8

BUILD 3- PERFORMANCE RESULTS

Temp. °F	Load	Cell #	Sep.	% SO_2	Li/SO_2	C/SO_2*	Time to 2.0V Hours	Peak V	SO_2 Eff. to 2.0V %	C - Ahr/gm to 2.0V
-20	2A	DR1	Dbl	72	1.01	.915	1.2	2.36	22.4	.35
-20	2A	DR2	Dbl	72	1.03	.98	1.3	2.40	24.3	.36
-20	2A	DR5	Dbl	72	1.02	.98	1.3	2.42	24.3	.36
-20	2A	DR6	Dbl	68	1.09	1.04	1.7	2.47	33.7	.46
-20	2A	DR7	Dbl	68	1.11	1.03	1.8	2.50	36.4	.51
-20	2A	DR8	Dbl	68	1.09	1.05	1.5	2.50	29.4	.41
-20	2A	DR9	Dbl	68	1.08	1.03	1.7	2.50	33.7	.47
-20	2A	WR2	Dbl	72	1.00	.89	1.2	2.38	22.4	.36
-20	2A	WR6	Dbl	72	1.02	.94	1.2	2.40	22.4	.34
-20	2A	WR7	Dbl	68	1.12	.94	1.3	2.45	25.7	.39
-20	2A	WR10	Dbl	68	1.11	.95	1.6	2.50	31.3	.48
-20	2A	WR11	Dbl	68	1.09	.94	1.2	2.50	24.0	.37
-20	2A	WR15	Sgl	72	1.08	.83	1.0	2.48	19.0	.33
-20	2A	WR16	Sgl	72	1.07	.87	0.9	2.39	17.0	.28
-20	2A	WR17	Sgl	72	1.06	.83	1.0	2.40	18.7	.33
-20	2A	WR1	Dbl	72	1.05	.92	1.1	2.37	21.0	.33
-20	2A	WR9	Dbl	72	1.05	.91	1.0	2.38	19.2	.30
-20	2A	WR12	Dbl	72	1.05	.88	1.0	2.40	19.2	.31
RT	2A	DR3	Dbl	72	.96	.95	3.9	2.75	72.9	1.07
RT	2A	DR10	Dbl	68	1.09	1.01	3.6	2.75	71.3	1.01
RT	2A	DR11	Dbl	68	1.08	1.05	3.8	2.72	75.2	1.03
RT	2A	WR4	Dbl	72	1.01	.94	3.4	2.79	63.5	.97
RT	2A	WR5	Dbl	72	1.01	.93	4.0	2.76	75.5	1.16
RT	2A	WR14	Dbl	68	1.10	.87	3.1	2.73	61.1	1.02
RT	2A	WR19	Sgl	72	1.07	.88	3.1	2.75	59.6	.98
RT	2.67Ω	DR4	Dbl	72	1.02	.98	8.5	2.78	79.4	1.16
RT	2.67Ω	WR3	Dbl	72	1.01	.94	8.2	2.78	76.6	1.17
RT	2.67Ω	WR13	Dbl	68	1.06	.98	8.2	2.78	81.2	1.19
RT	2.67Ω	WR18	Sgl	72	1.04	.86	8.5	2.79	79.4	1.33

* Based on 1.44 Ahr/g mix theoretical.

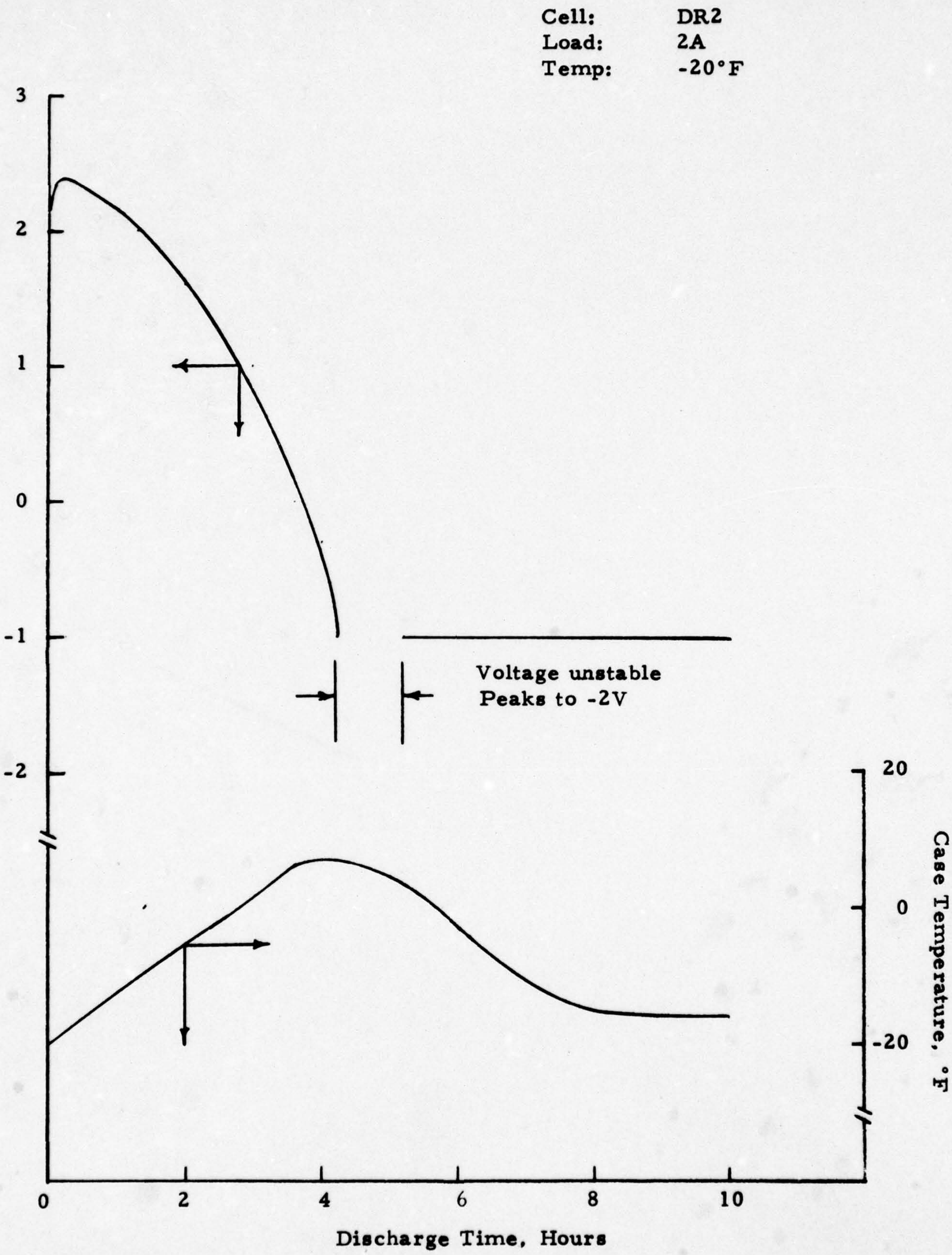

Figure 8. Performance/Safety Test

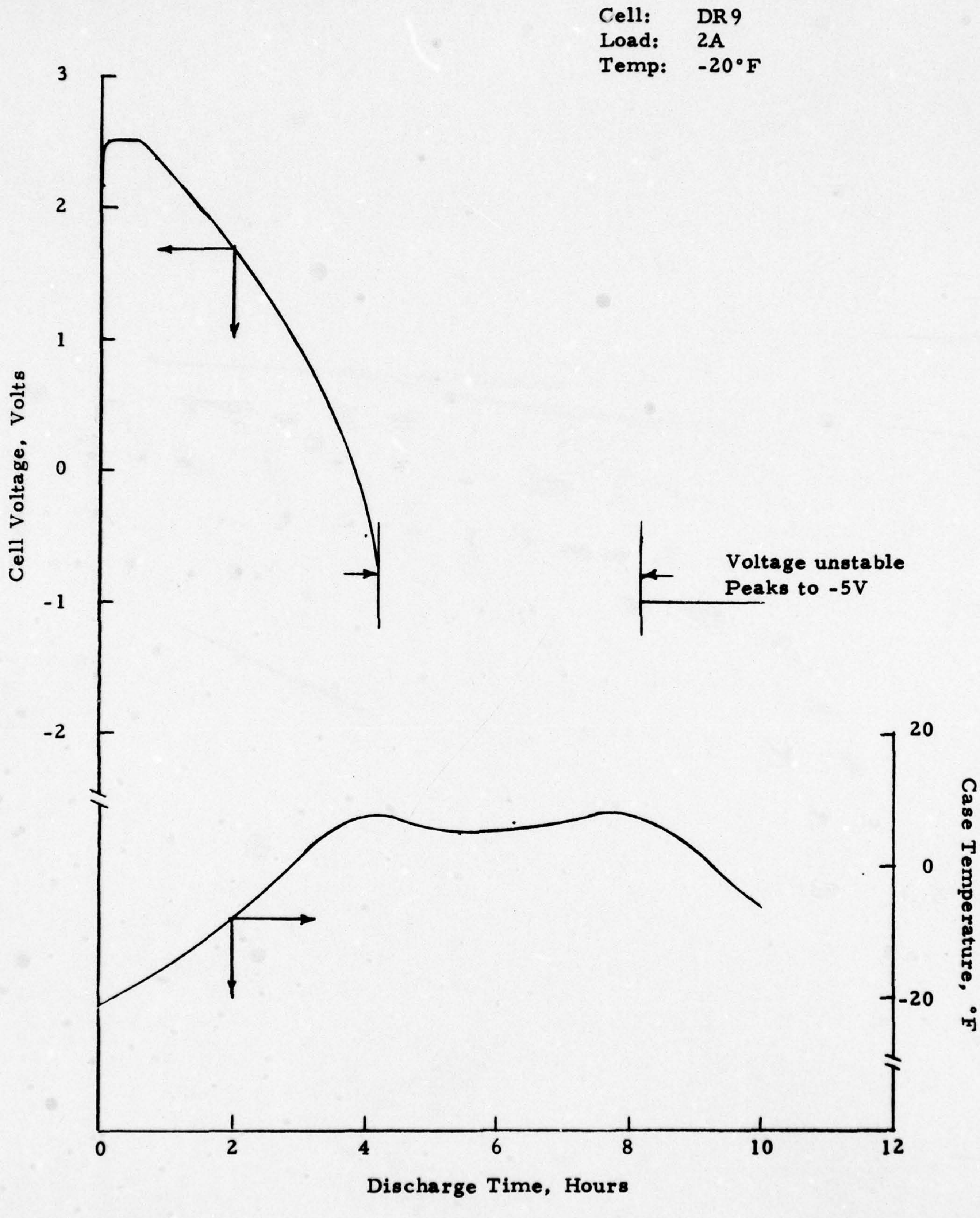

Figure 9. Performance/Safety Test

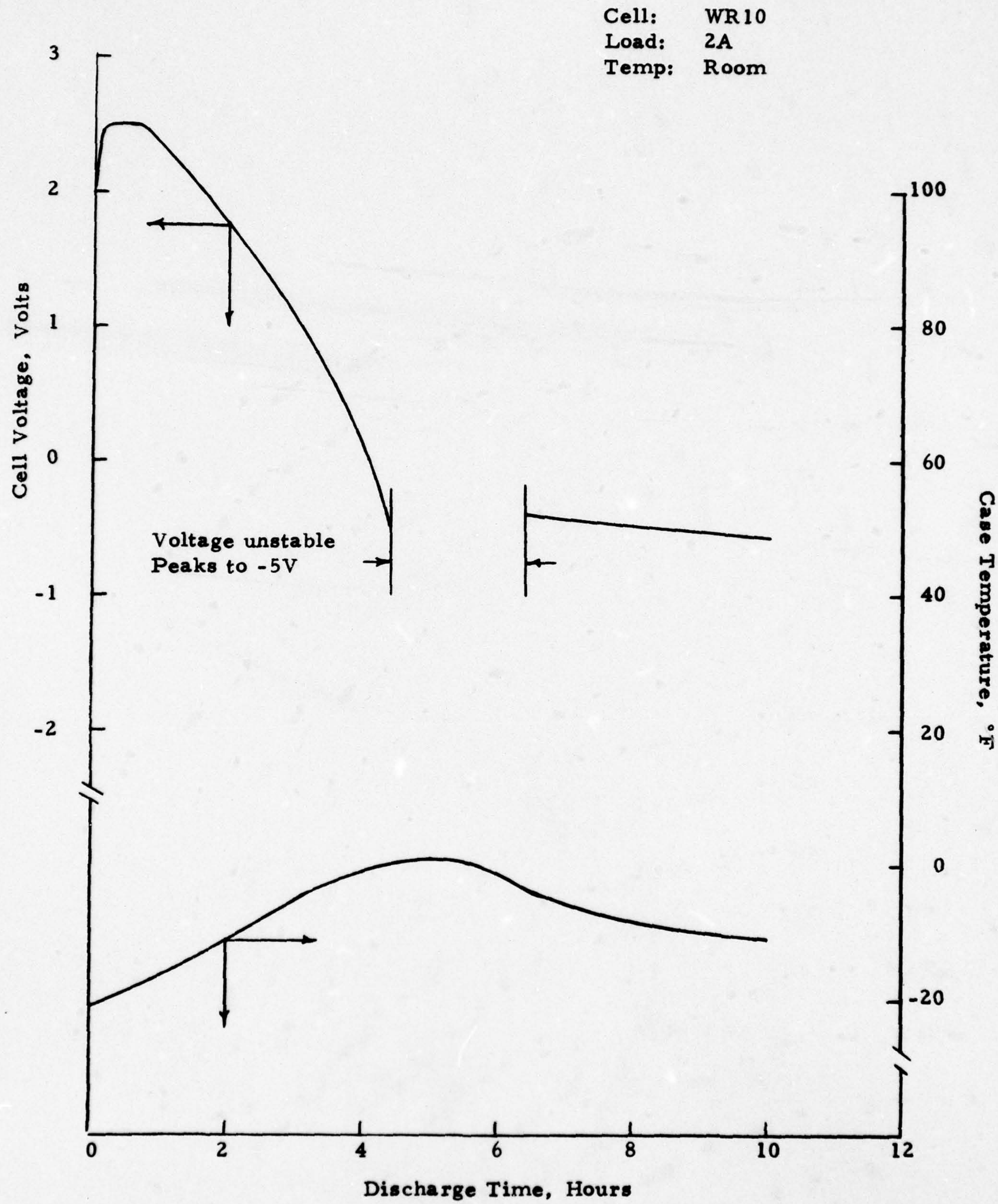

Figure 10. Performance/Safety Test

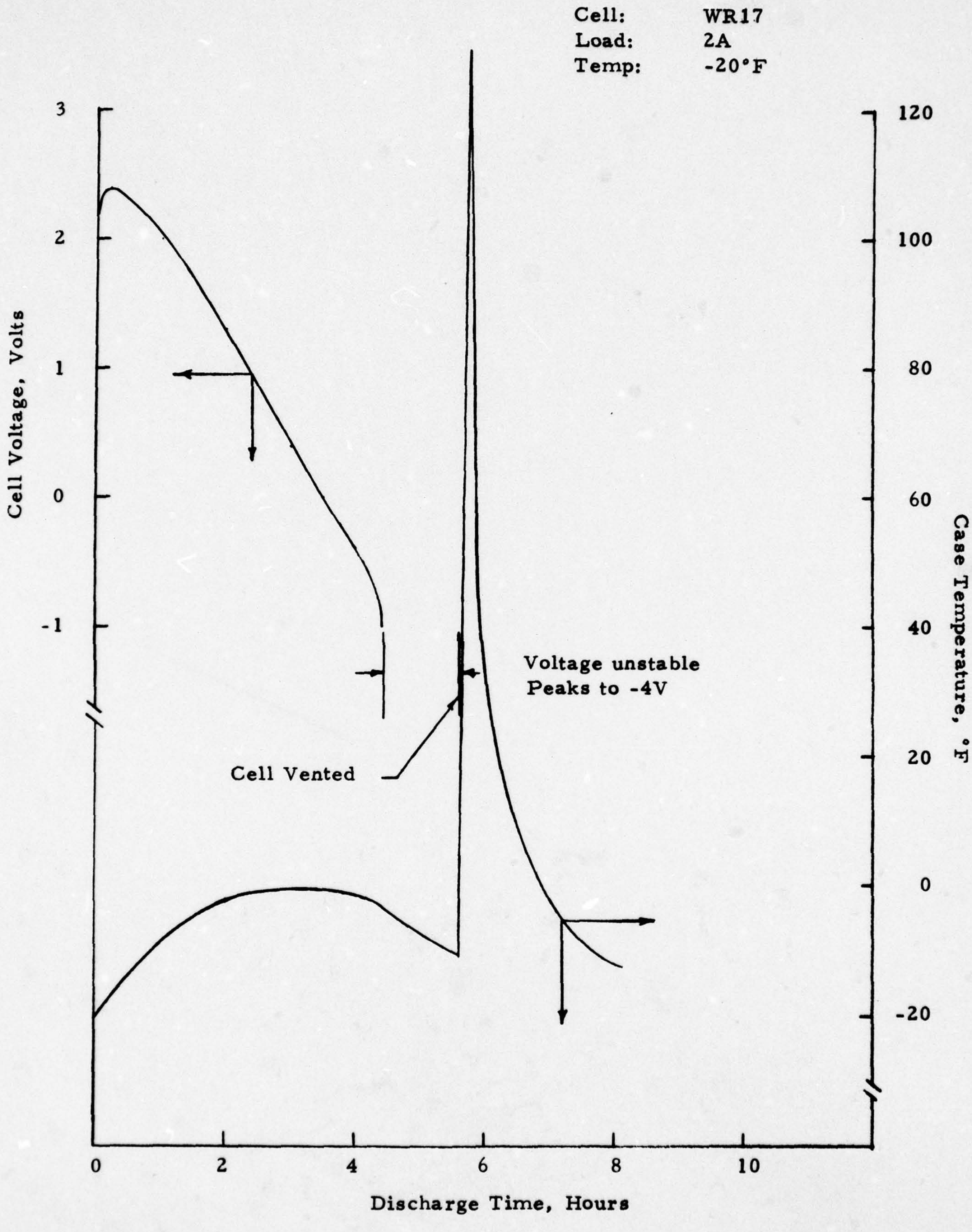

Figure 11. Performance/Safety Test

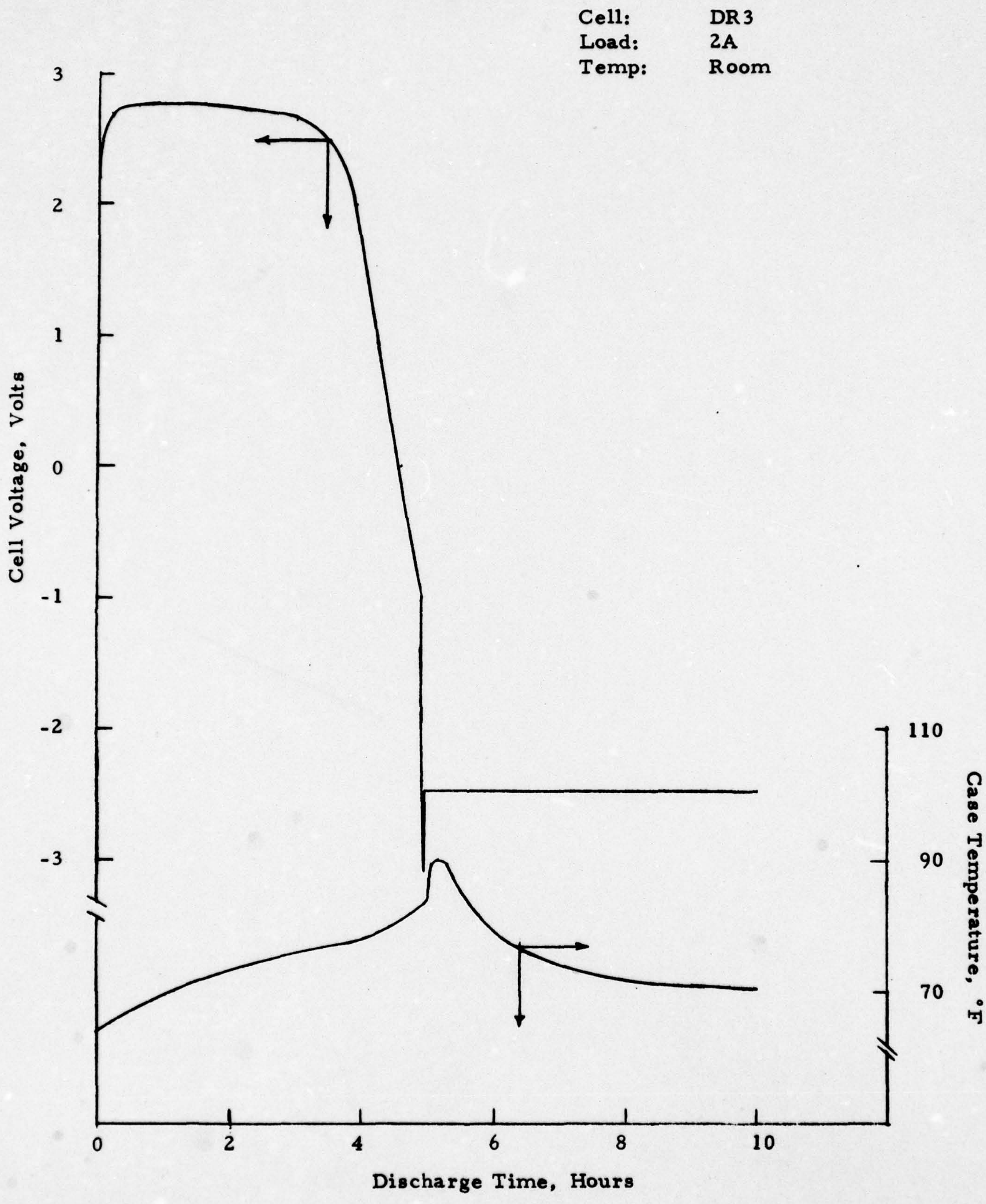

Figure 12. Performance/Safety Test

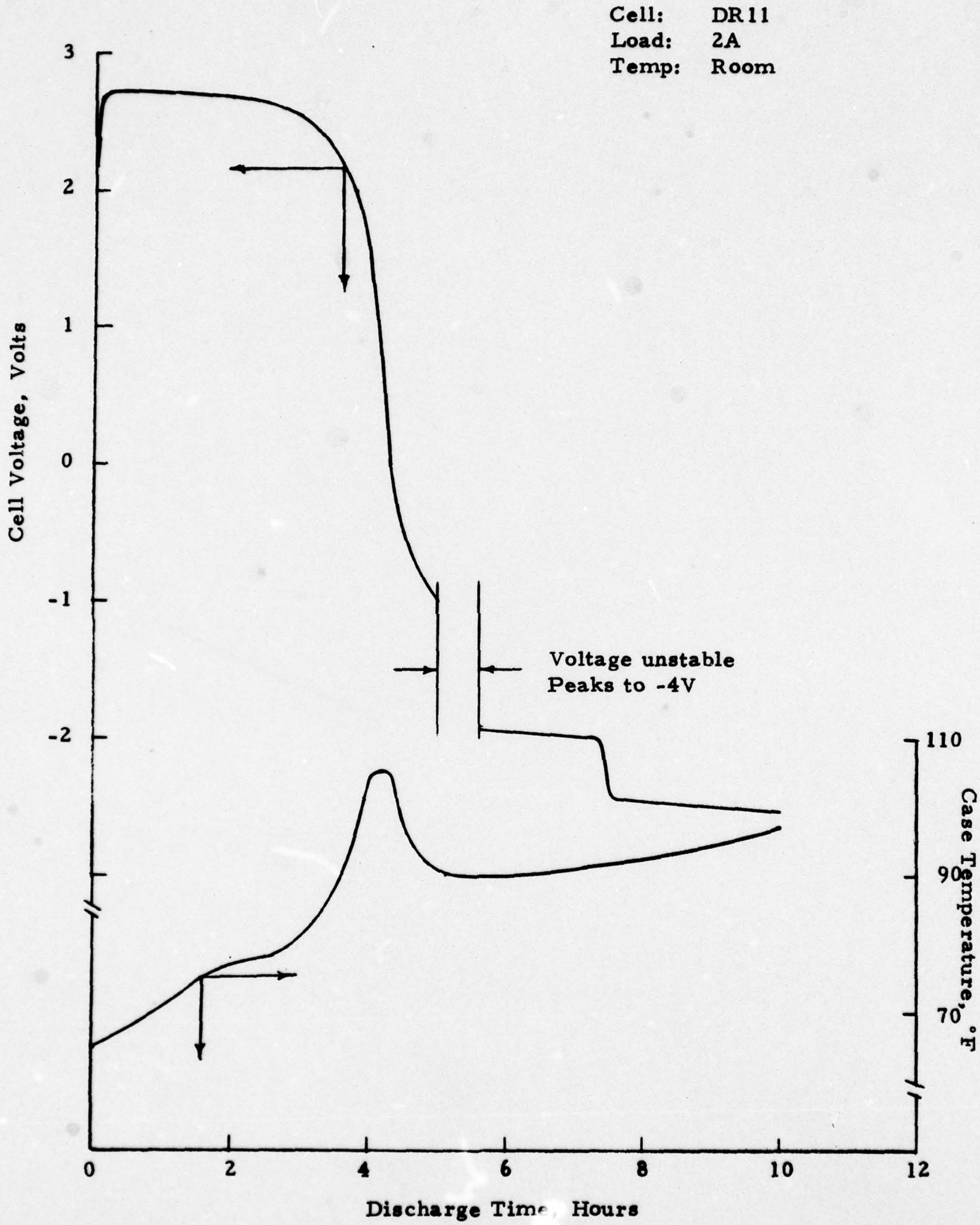

Figure 13. Performance/Safety Test

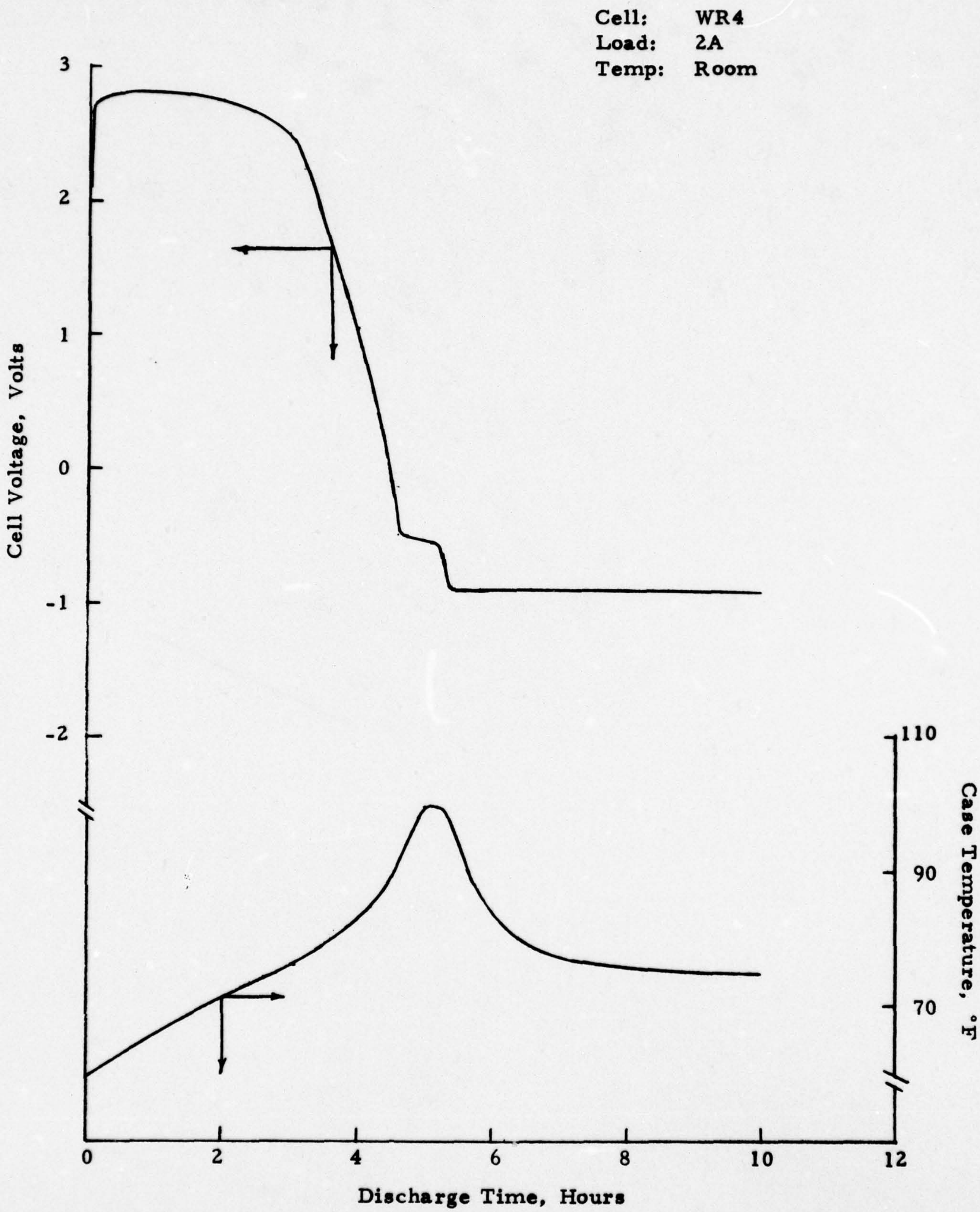

Figure 14. Performance/Safety Test

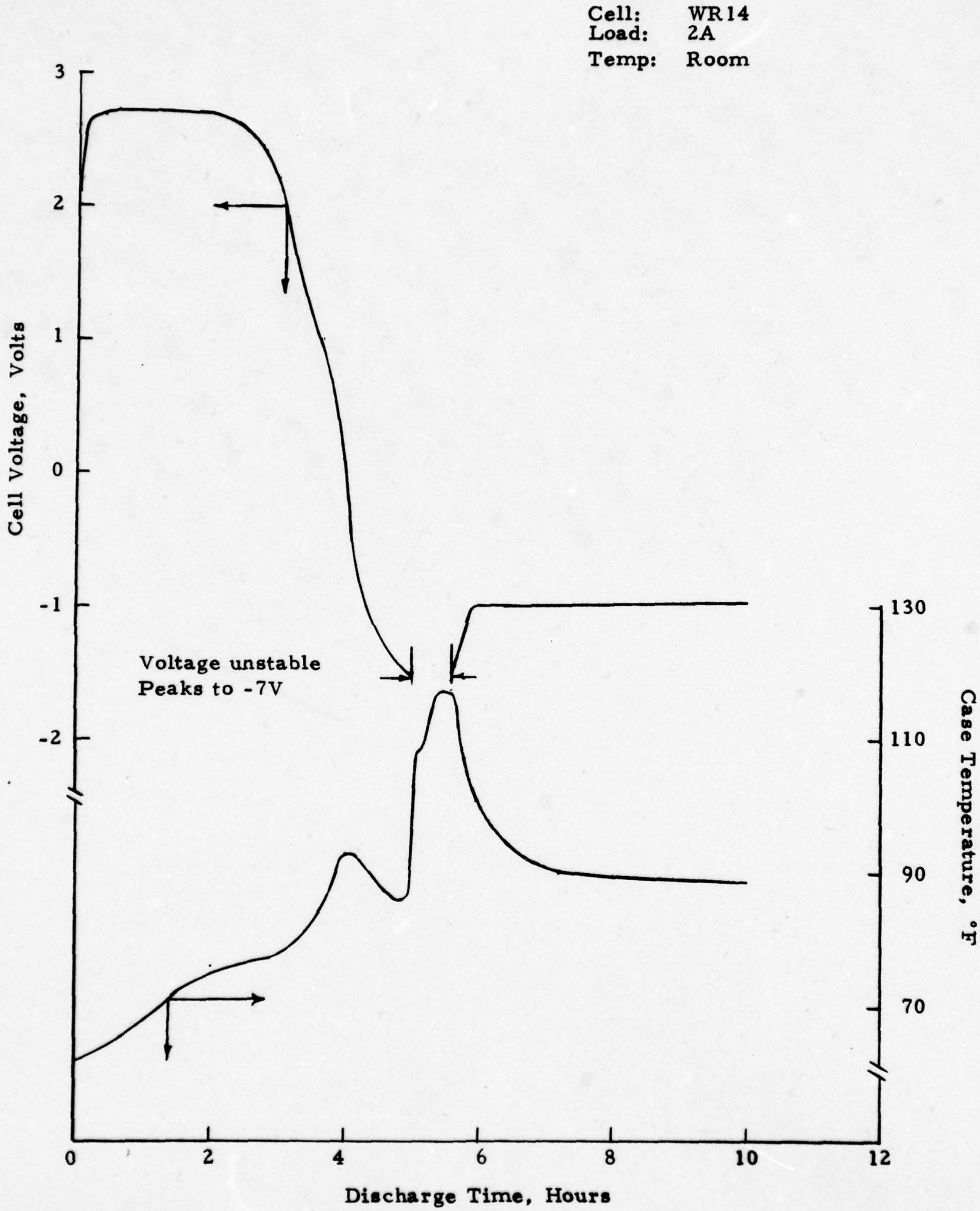

Figure 15. Performance/Safety Test

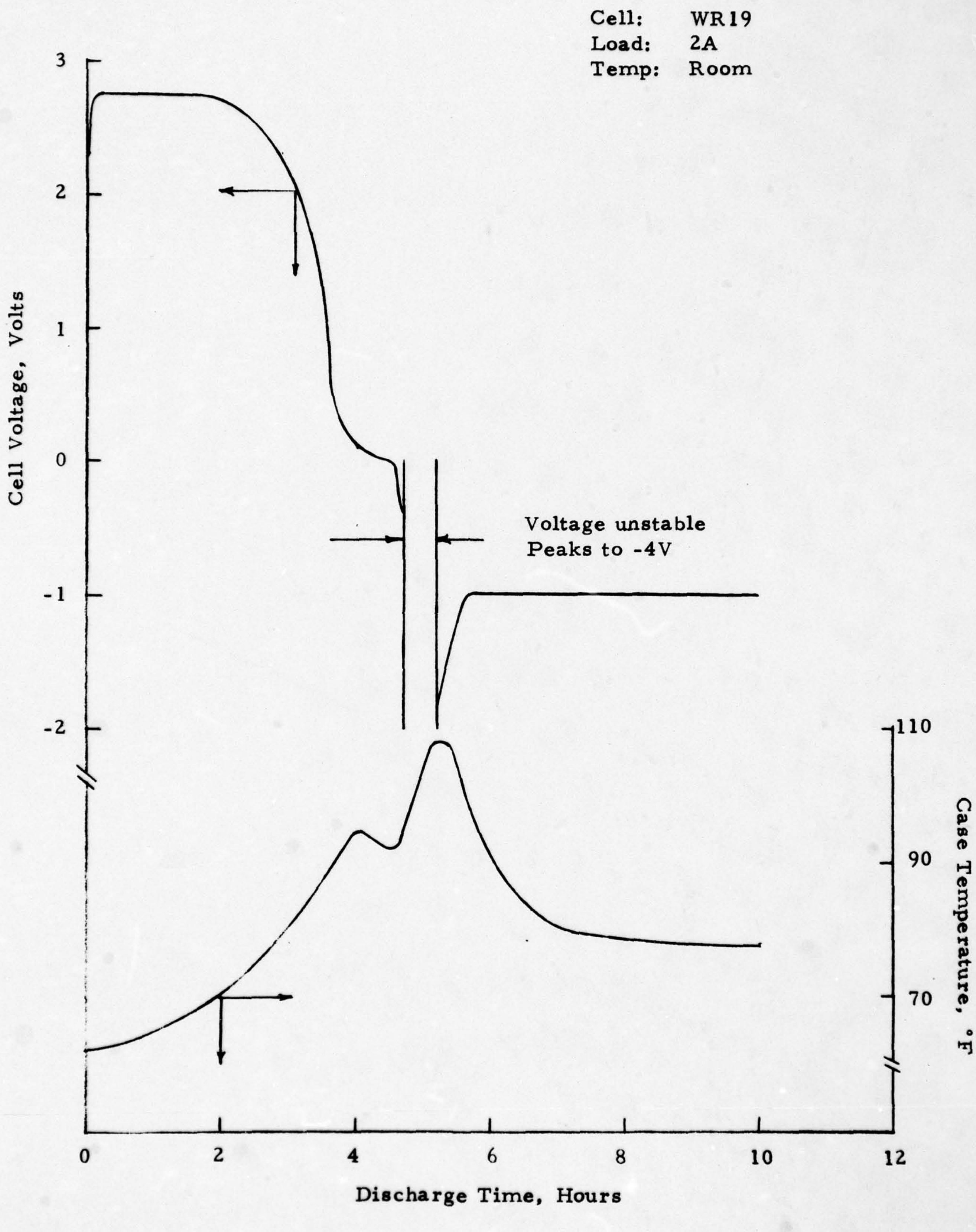

Figure 16. Performance/Safety Test

tion and a low density, 0.035 inch cathode while the latter increased the carbon loading by 20-30% by eliminating one separator layer and densifying the mix in the rolling process. All cells were filled with 68% SO_2 electrolyte to a design capacity of 10.7 Ah. Comparison of design parameters to other builds is shown in Table 7.

The cells were again stored for 48 hours at 165°F before testing. The 2A discharge tests showed a major difference in both discharge efficiency and safety between the two groups of cells. Table 9 shows the lower density, 2 layer separator cells discharged poorly, especially at room temperature, while the high density single separator cells performed exceptionally well, meeting the 2.0 hour -20°F goal in two of the four cells tested. It should be noted the two cells with the highest carbon/teflon loadings, DR25 and DR24, achieved the best results at 2.0 and 3.9 hours for -20°F and room temperature respectively.

The safety results, Table 10, followed hand-in-hand with the discharge efficiency. The poor performing low density cathode cells were susceptible to venting on extended discharge with one cell even venting with flame. All eight of the good performers (4 at -20°F, 4 at room temperature) on the other hand remained unvented for the 10 hour 2A discharge. Figures 17 to 20 trace the voltage and temperature profiles of representative cells during the discharge testing. Unstable voltage conditions were apparent in all cells to varying degrees after the cells were driven negative. Unexplained temperature excursions were also noted in some cells during the negative voltage portion of the discharge.

TABLE 9

BUILD 4 - PERFORMANCE RESULTS

Electrolyte: 68% SO_2
Load : 2 A

Temp., °F	Cell No.	Layers of Separator	C & Tef gm/cc	Li/SO_2	C/SO_2 *	Time to 2.0 V Hours	Peak, V	SO_2 Eff. to 2.0 V, %	C & Tef Ah/gm to 2.0V
-20	DR14	2	0.26	0.88	0.92	1.4	2.32	26.1	0.41
	DR15	2	0.25	0.90	0.89	1.3	2.35	24.5	0.40
	DR19	1	0.33	1.05	1.10	1.8	2.50	34.0	0.44
	DR20	1	0.34	1.01	1.11	2.0	2.50	37.3	0.49
	DR21	1	0.33	1.01	1.08	1.5	2.39	28.0	0.37
	DR25	1	0.35	0.97	1.23	2.0	2.50	37.7	0.44
RT	DR12	2	0.24	0.87	0.86	1.6	2.68	30.2	0.51
	DR13	2	0.24	0.88	0.84	2.0	2.73	37.7	0.65
	DR16	2	0.26	0.89	0.91	2.3	2.70	43.4	0.69
	DR18	1	0.33	0.98	1.15	3.8	2.80	71.0	0.90
	DR22	1	0.32	1.03	1.12	3.7	2.80	69.2	0.89
	DR23	1	0.34	1.04	1.15	3.7	2.76	69.8	0.87
	DR24	1	0.34	1.03	1.20	3.9	2.78	73.6	0.88

* Based on 1.44 Ahr/gm mix theoretical.

TABLE 10

BUILD 4 - SAFETY RESULTS

Chamber Temperature °F	Cell No.	Time to Vent at 2.0A, hrs	Case Surface Temp, °F	Flame on Venting
R/T	DR-12	4.0	250	Yes
	DR-16	4.2	110	No
	DR-18	No Vent		
	DR-22	"		
	DR-23	"		
	DR-24	"		
-20°F	DR-14	7.3	41	No
	DR-15	No Vent		
	DR-19	No Vent		
	DR-20	"		
	DR-21	"		
	DR-25	"		

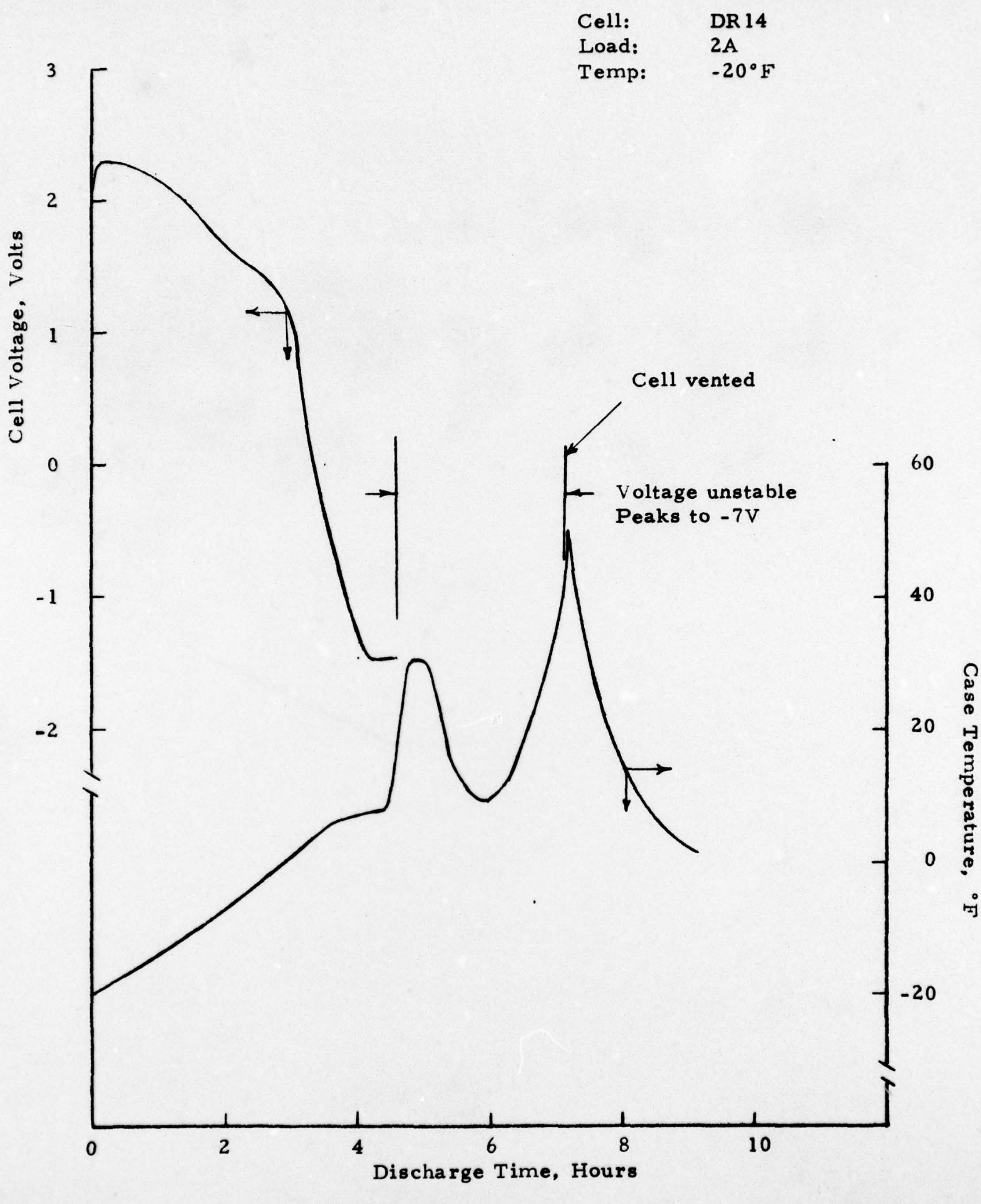

Figure 17. Performance/Safety Test

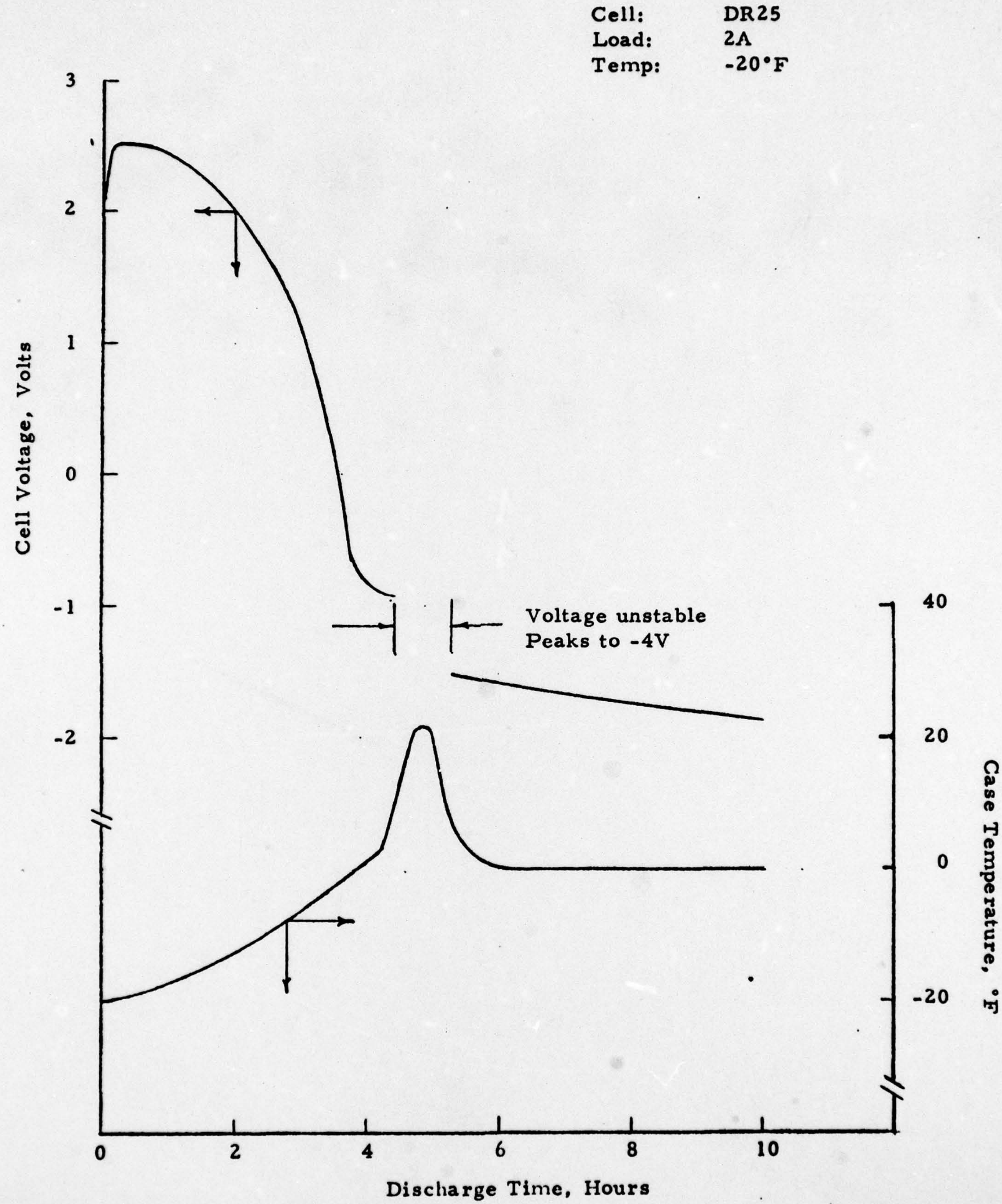

Figure 18. Performance/Safety Test

Cell: DR12
Load: 2A
Temp: Room

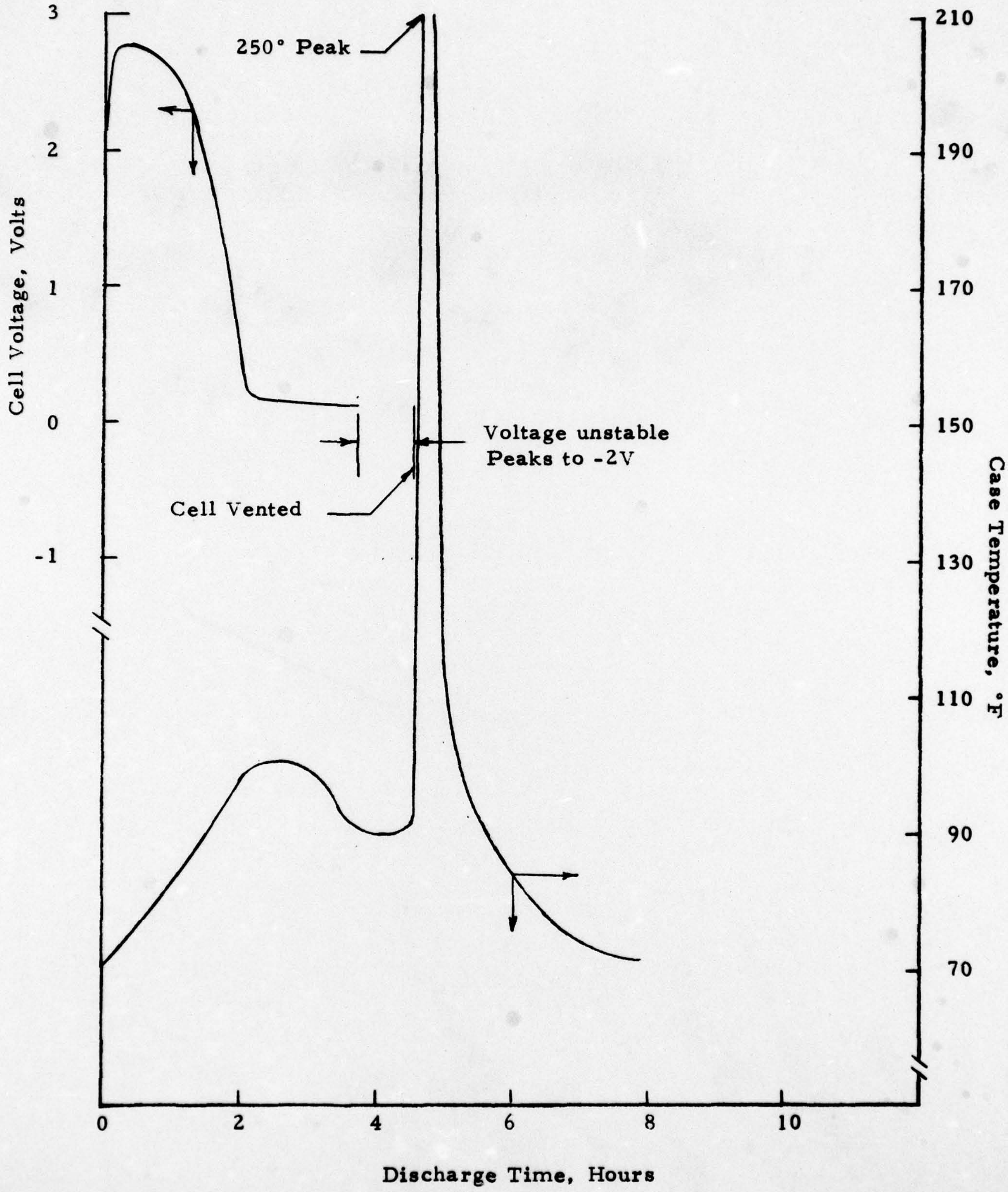

Figure 19. Performance/Safety Test

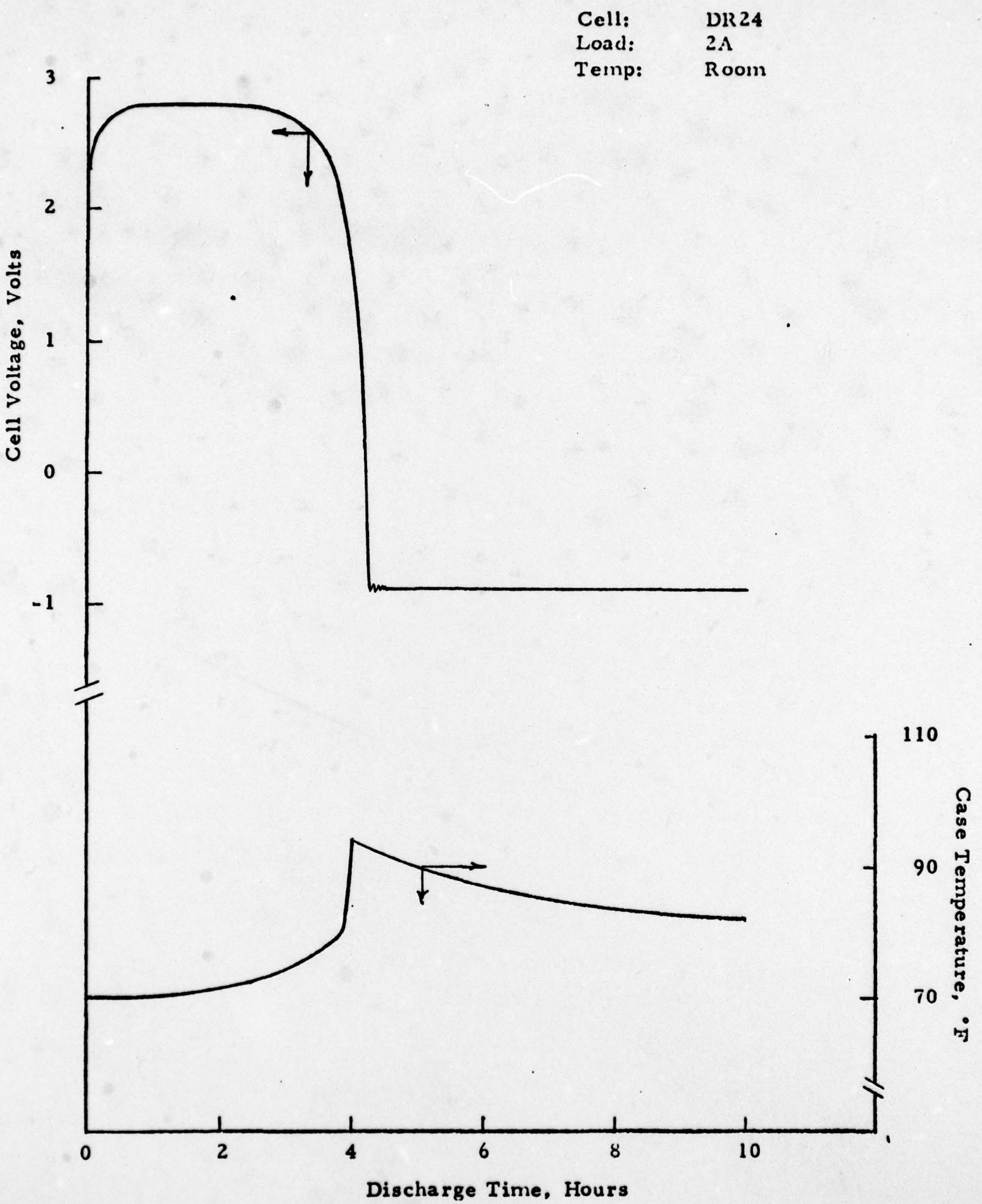

Figure 20. Performance/Safety Test

4.0 DISCUSSION

In the short time frame of the program and the added task of upgrading a low rate design, a statistical approach to optimize the design for safe operation was not practical. Instead, multiple parameters were varied and the number of replications limited with promising variables retained for subsequent builds. With this systematic approach, progress toward a safe and efficient cell was accomplished but without statistical confidence to the significance of each variable.

Within the scope of the testing, discharge efficiency appeared to have one of the strongest effects on safety. Several design changes improved the discharge efficiency but most significant was the development of a high rate cathode. Examination of the data as summarized in Table 11 indicates the carbon loading has a direct bearing on the efficiency. Graphing the carbon loading in terms of the carbon mix weight against the delivered capacity to 2.0V, figures 21 and 22, shows a definite trend towards increased capacity with increased loadings. The improvement appears to taper at the higher loadings but this can be expected as the density increases and the cathode becomes less porous. Build-to-build scatter in the data indicates parameters other than cathode loading and SO_2 concentration are affecting cell operation. Likely are surface area, cathode processing, separator changes and material and assembly variations; the latter variation being evident from the scatter within individual builds.

Considering the above analysis, the reduction of the teflon content from 20 to 5% improved the performance and resulting safety mainly by increasing the carbon content and efficiency. Plotting the 20% teflon cells from build 1 on Figures 21 and 22, by adjusting the carbon mix weights to 5% teflon, shows they follow the pattern of later builds, thus explaining their poor performance, especially at -20°F. Other possible effects, not apparent from the graphs, are the increase in cathode porosity and conductivity from the reduction of teflon content.

TABLE 11

BUILD SUMMARY - REVERSE WRAP DESIGN

							-20°F				Room Temperature			
Bld.	Area cm^2	Cathode % Tef. Type	Sep.	% SO_2	Li/SO_2	C/SO_2 *	Time to 2.0V	Peak V	SO_2 Eff.	C & Tef Ahr/gm 2.0V	Time to 2.0V	Peak V	SO_2 Eff.	C & Tef Ahrs/gm 2.0V
1	630	20 Slurry	2	72	1.20	.83	.65	2.38	12	.20	3.3	2.70	62	1.05
2	493	5 Slurry	2	72	.99	.94	1.2	2.35	22	.33	3.4	2.73	66	1.00
	493	5 Wet Roll	2	72	.99	.96	1.3	2.35	25	.38	4.0	2.75	78	1.13
3	605	5 Wet Roll	2	72	1.02	.89	1.2	2.42	22	.36	3.7	2.77	70	1.07
	605	5 Wet Roll	2	68	1.11	.94	1.4	2.50	27	.43	3.1	2.73	61	1.02
	605	5 Wet Roll	1	72	1.07	.85	1.0	2.45	18	.30	3.1	2.75	60	.98
	605	5 Dry Roll	2	72	1.02	.95	1.3	2.40	23	.36	3.9	2.75	73	1.07
	605	5 Dry Roll	2	68	1.10	1.04	1.7	2.50	34	.47	3.7	2.73	73	1.02
4	540	5 Dry Roll	2	68	.87	.90	1.4	2.33	25	.41	2.0	2.70	38	.65
	580	5 Dry Roll	1	68	1.00	1.15	1.8	2.50	36	.46	3.8	2.80	71	.88

* Based on 1.44 Ahr/gm mix theoretical.

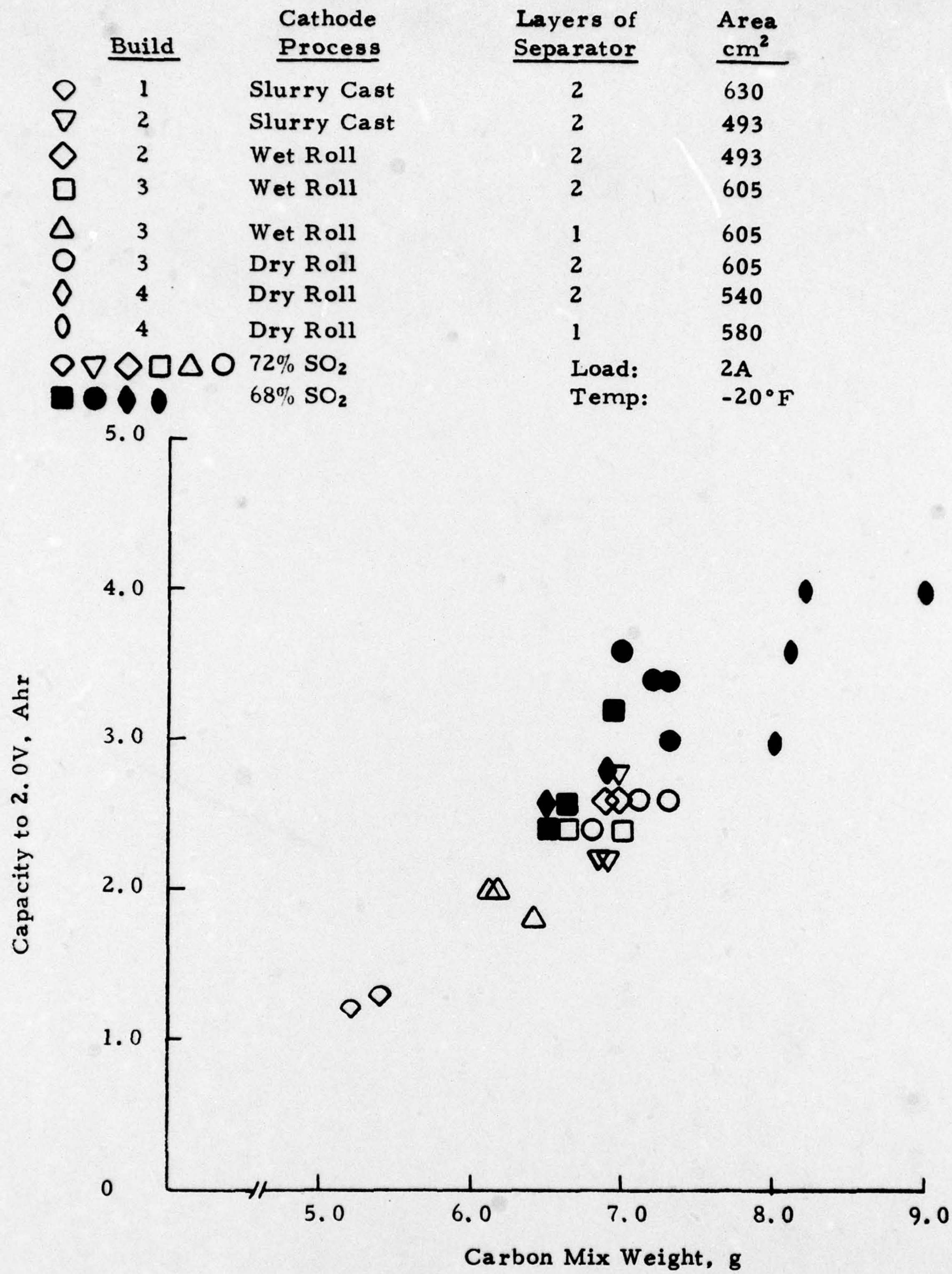

Figure 21. Cathode Comparison at -20°F

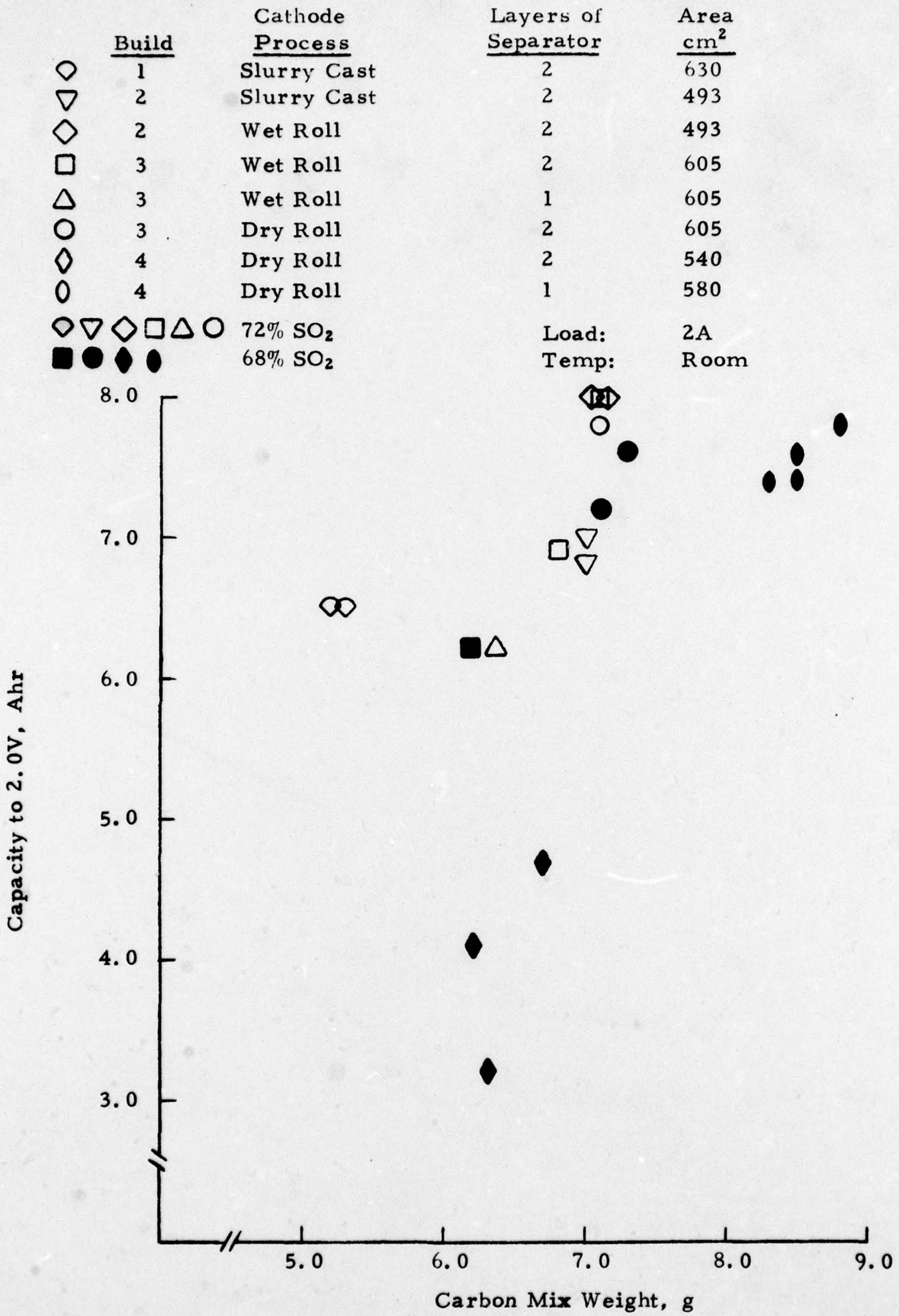

Figure 22. Cathode Comparison at Room Temperature

The effect of the SO_2 concentration is clearly shown from Figures 15 and 16. Decreased SO_2 concentrations decrease room temperature efficiency while increasing -20°F efficiency. Cells with the higher loading and 68% SO_2 delivered better than 90% of the desired capacity at both temperatures fixing a concentration of 68% SO_2 as close to optimum.

Other possible influences on discharge efficiency are surface area, separator thickness, lithium content and cathode porosity. The carbon loadings appear to overshadow the effects of the first two as Figures 15 and 16 again illustrate. With regard to lithium content, the diagonal anode lead should compensate for uneven lithium depletion and no significant effect on discharge efficiency was expected even at the low 0.87 Li/SO_2 ratio of some of the build 4 cells. The cause of the poor performance and safety from these cells is not fully evident from the data. However, the low density of the cathodes from these particular cells (0.25 g/cc compared to 0.30 - 0.36 g/cc from other cells) may have contributed and this new variable should be considered for future work.

Previous studies (1) have shown that lithium content has a bearing on safe operation when discharged into voltage reversal. Therefore, the lithium content was lowered and the trend was toward less frequent and less violent venting. Since discharge efficiency was improving during this time, it was difficult to quantitatively separate the cause and effect relationships. Cells from builds 3 and 4 with Li/SO_2 ratios as high as 1.1 and in conjunction with good discharge efficiences were shown to be safe.

This program was successful in improving the safety of high rate SO_2 cells. Design trade-offs yielded a reasonable discharge efficiency and a non-venting condition during extended discharge to 200% of the theoretical SO_2 content. Further work is needed to statistically confirm these findings and determine the full impact and range of the variables influencing safety. If discharge efficiency is the key to safety, further optimization, especially for the cathode is warranted. In addition, utilization of internal cell heating could improve discharge efficiency and this condition is more representative of actual battery application. Manufacturing, quality control and reliability would become most critical and safeguards against poor components, especially the seal, to prevent low discharge efficiency would have to be developed.

5.0 REFERENCES

(1) G. DiMasi, Proc. 26th Power Sources Symposium, Atlantic City (1974) p. 75.

6.0 ACKNOWLEDGEMENTS

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